

# Octahedral Bis(2-picolylamine) Complexes of Cobalt(III)

## Preparations and Partial Structural Assignments of Two Series of Isomers

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Compounds belonging to two of the three possible series of cobalt(III) complexes of the general formula  $cis\text{-}[\text{Co}(\text{C}_6\text{H}_5\text{N}_2)_2\text{X}_2]^{n+}$ , where  $\text{X} = \text{NO}_2$ ,  $\text{Cl}$ ,  $\text{H}_2\text{O}$ , and  $\text{NH}_3$ , have been prepared for the first time, and their absorption spectra have been measured.

The  $^1\text{H}$  NMR spectra show, that the compounds belonging to the so-called  $\beta$ -series apparently contain completely unsymmetrical complex ions, while the compounds belonging to the  $\alpha$ -series evidently contain cations with a two-fold axis of symmetry.

Compounds with the monodentate ligands in the *trans* positions were never observed.

### 1. INTRODUCTION

As mentioned in an earlier paper on complexes of chromium(III) and cobalt(III) with the bidentate ligand 2-picolylamine (2-aminomethylpyridine)<sup>1</sup> previous interest in this topic is scarce. The work on cobalt complexes seems in the main to have been concerned with the determination of formation constants for complexes of cobalt(II).<sup>2,3</sup> No complexes seem to have been isolated. Yet it should be mentioned, that Utsunu<sup>4</sup> recently prepared cobalt(II) complexes with the related 6-methyl-2-aminomethylpyridine.

This work describes suitable synthetic methods for the preparations of octahedral bis(2-picolylamine) complexes of cobalt(III). The ligands in the *cis* positions are  $\text{NO}_2^-$ ,  $\text{Cl}^-$ ,  $\text{H}_2\text{O}$ , and  $\text{NH}_3$ . The compounds are characterized by their absorption spectra in the visible region. Their  $^1\text{H}$  NMR spectra are used to give a partial structural assignment of the isomers. Although there seems to be no reason, why they should not exist, complexes with the monodentate ligands  $\text{X}$  in the *trans* positions were not observed during the experiments. This is in contrast to the observations made in this laboratory with the corresponding chromium compounds.<sup>5</sup>

## 2. GENERAL CONSIDERATIONS

2-Picolylamine lacks a two-fold axis of symmetry. Consequently three geometrical isomers of the *cis* complexes occur, namely a *cis, trans, cis*, a *cis, cis, trans*, and a *cis, cis, cis* isomer (Fig. 1). The isomers are named by considering first the spatial relationship of the two monodentate ligands, then of the two pyridine-nitrogen atoms and finally of the two methylamine-nitrogen atoms. There is no obvious reason (as for instance sterical hindrances), why all three isomers should not exist, but nevertheless it was only possible to prepare compounds belonging to two series, called  $\alpha$  and  $\beta$ . Oddly enough it has also been possible to prepare the corresponding two chromium series<sup>5</sup> (isomorphism is proved by X-ray powder photographs), while compounds belonging to the third did not appear.

One should expect, that the <sup>1</sup>H NMR spectra for complexes of at least one of the two series should reveal the existence of a twofold axis of symmetry, and so it did. The data for the so-called  $\alpha$ -complexes gave evidence of this symmetry, thus assigning a *cis, trans, cis* or a *cis, cis, trans* configuration to this group. The spectra, of course, could not show whether the configuration was as in Fig. 1a with the pyridine-nitrogens in the *trans* positions, or as in

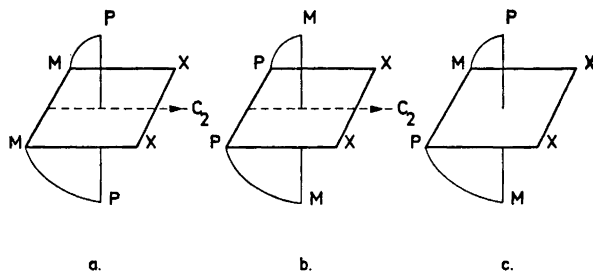


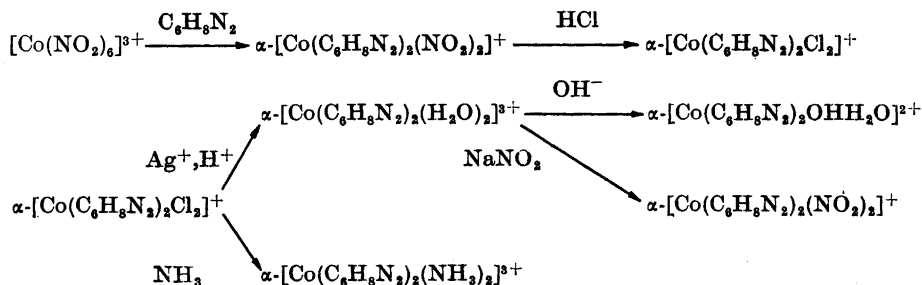
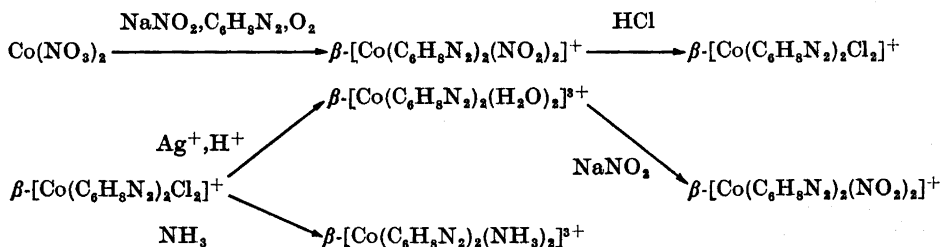
Fig. 1. The geometrical isomers of the *cis*- $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2\text{X}_2]^{n+}$  ion. P symbolizes the pyridine nitrogens, M the methylamine nitrogens. a. The *cis, trans, cis* isomer. b. The *cis, cis, trans* isomer. c. The *cis, cis, cis* isomer.

Fig. 1b with the methylamine-nitrogens in the *trans* positions. For the time being this question must be left open, but experiments are carried out to answer it. The <sup>1</sup>H NMR spectra for the  $\beta$ -series revealed a complete lack of symmetry, thus assigning a *cis, cis, cis* configuration as in Fig. 1c to the members of this group.

## 3. GENERAL REMARKS CONCERNING THE PREPARATION METHODS

The preparations do not contain any new or sensational methods. They have all been used in the syntheses of related compounds as for instance complexes with ethylenediamine. Yet they include interesting traits as the fact, upon which this whole work is based, namely that the reaction between sodium or potassium hexanitrocobaltate(III) and 2-picolylamine mainly gives the

so-called  $\alpha$ -[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]NO<sub>2</sub>, while the oxidation of cobalt(II) nitrate in the presence of sodium nitrite and 2-picolyamine chiefly results in  $\beta$ -[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]NO<sub>3</sub>. All the other preparations are based on these two initial products, as appears from the reaction schemes below. The first method was used by Werner and Humphrey<sup>6</sup> to prepare *cis*-[Coen<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]NO<sub>2</sub> and the second by Holtzclaw *et al.*<sup>7</sup> to prepare *trans*-[Coen<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]NO<sub>3</sub>.

 $\alpha$ -Series $\beta$ -Series

*cis*-[Coen<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]NO<sub>2</sub> reacts with conc. hydrochloric acid to form *trans*-[Coen<sub>2</sub>Cl<sub>2</sub>]Cl.  $\alpha$ -[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]NO<sub>2</sub> and  $\beta$ -[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]NO<sub>3</sub> both form *cis*-complexes of the general formula *cis*-[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>]Cl. The aqua complexes are prepared by the reaction of the chloro complexes with silver oxide (followed by an acidifying of the filtrate) or with silver nitrate. A similar method was used by Bjerrum and Rasmussen,<sup>8</sup> when they prepared *trans*-[Coen<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>3</sub>. The addition of pyridine to a conc. solution of  $\alpha$ -*cis*-[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]Cl<sub>3</sub> in water resulted in the formation of  $\alpha$ -*cis*-[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>OHH<sub>2</sub>O]Cl<sub>2</sub>. The method is classical,<sup>9</sup> but not successful, when used to provide the corresponding  $\beta$ -complex from  $\beta$ -*cis*-[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]Br<sub>3</sub>. The isolated compound always appears as a sticky, impure product. The reaction between liquid ammonia and  $\alpha$ - and  $\beta$ -*cis*-[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>]Cl to yield the corresponding ammine complexes is related to the method by which Bailar *et al.*<sup>10</sup> prepared *l*- and *d*-*cis*-[Coen<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]Cl from *l*- and *d*-*cis*-[Coen<sub>2</sub>Cl<sub>2</sub>]Cl.

## 4. EXPERIMENTAL

*Reagents.* 2-Picolylamine was purchased from Aldrich Co. All other reagents were of reagent grade and used without further purification.

## Preparations

1.  $\alpha$ -*cis*-Dinitrobis(2-picolylamine)cobalt(III) nitrate,  $\alpha$ -[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]NO<sub>2</sub>. 4.0 g Na<sub>3</sub>[Co(NO<sub>2</sub>)<sub>6</sub>] (10 mmol) was dissolved in 40 ml water (20°C). A solution of 2.0 ml 2-picolylamine (20 mmol) in 10 ml water was added dropwise during 15 min. A red-orange precipitate soon formed, but gradually disappeared giving place to yellow crystals. After stirring for further half an hour and cooling on ice, the lemon yellow crystals were filtered and washed with ice-cold water and acetone. The crude product was extracted on the filter with approx. 70 ml boiling water. By cooling on ice, 3.1 g of shining crystals separated. Washing as above. The nitrite was recrystallized by dissolving in 60 ml boiling water and cooling of the filtrate. Yield: 2.9 g (67 %). (Found: Co 13.74; C 33.1; N 22.7; H 4.23. Calc. for [Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]NO<sub>2</sub>·H<sub>2</sub>O: Co 13.67; C 33.4; N 22.7; H 4.21.) ( $\epsilon, \lambda$ )<sub>max</sub>: (296, 438.5). ( $\epsilon, \lambda$ )<sub>min</sub>: (260, 416).

The same product was obtained, when 4.6 g K<sub>3</sub>[Co(NO<sub>2</sub>)<sub>6</sub>] (10 mmol) suspended in water reacted with 2.0 ml 2-picolylamine (20 mmol). The temperature was maintained at 60° until a brown-yellow precipitate appeared (approx. 1 h). After cooling on ice the crystals were filtered and then treated exactly as described above. Yield of pure [Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]NO<sub>2</sub>·H<sub>2</sub>O: 2.0 g (46 %).

2.  $\alpha$ -*cis*-Dichlorobis(2-picolylamine)cobalt(III) chloride,  $\alpha$ -[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>]Cl. 2.15 g  $\alpha$ -[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]NO<sub>2</sub>·H<sub>2</sub>O (5.0 mmol) was suspended in a few ml conc. hydrochloric acid. A red-orange bulky precipitate immediately formed, presumably [Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(NO<sub>2</sub>)Cl]Cl. The mixture was heated on a water-bath (100°), whereby a dark-red solution arised. The solution was evaporated to dryness. The final red-violet product was treated on a glass-filter with acetone and afterwards extracted with 40 ml boiling water. The filtrate was cooled on ice, and a solution of 4 g lithium chloride in 50 ml ethanol was added. Red-violet crystals separated. They were filtered and washed with ethanol and acetone; 1.7 g. The recrystallization was performed by dissolving the crystals in approx. 35 ml boiling water and precipitating the crystals from the filtrate with lithium chloride dissolved in ethanol as above. Washing with ethanol and acetone. Yield: 1.5 g (75 %). (Found: Co 14.76; C 36.0; N 14.1; H 4.56; Cl 26.6. Calc. for [Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>]Cl·H<sub>2</sub>O: Co 14.75; C 36.1; N 14.0; H 4.54; Cl 26.6.) ( $\epsilon, \lambda$ )<sub>max</sub>: (136, 538.5). ( $\epsilon, \lambda$ )<sub>min</sub>: (20.3, 450). Half-width: 3333 cm<sup>-1</sup>.

3a.  $\alpha$ -*cis*-Diaquabis(2-picolylamine)cobalt(III) nitrate,  $\alpha$ -[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>3</sub>. 1.50 g  $\alpha$ -[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>]Cl·H<sub>2</sub>O (3.75 mmol) was dissolved in 15 ml water (80°). The solution was added to a solution of 2.4 g silver nitrate (14 mmol) in 5 ml water. The new-formed orange solution was filtered from the precipitated silver chloride and a few drops of 4 M nitric acid were added. During icecooling and stirring, 250 ml ethanol (99 %) was added slowly to precipitate orange crystals of presumed [Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>3</sub>. They were filtered and washed with ethanol (99 %) and acetone; 1.5 g. The recrystallization was performed by dissolving in 6 ml 1 M nitric acid (70°), filtering and reprecipitating during ice-cooling and stirring with 150 ml ethanol (99 %). Washing as above. Yield 1.40 g (75 %). (Found: Co 11.78; C 29.0; N 19.9; H 4.08. Calc. for [Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>3</sub>: Co 11.85; C 29.0; N 19.7; H 4.05.) ( $\epsilon, \lambda$ )<sub>max</sub>: (150, 489), (98.3, 353). ( $\epsilon, \lambda$ )<sub>min</sub>: (17.7, 408), (89.8, 335). Half-width: 3453 cm<sup>-1</sup>.

3b.  $\alpha$ -*cis*-Diaquabis(2-picolylamine)cobalt(III) hydrogensulfate-sulfate,  $\alpha$ -[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]HSO<sub>4</sub>·SO<sub>4</sub>. 1.00 g  $\alpha$ -[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>]Cl·H<sub>2</sub>O (2.5 mmol) was added to moist silver oxide, freshly prepared from 2.4 g silver nitrate (14 mmol). The violet solution was filtered from silver chloride and surplus silver oxide and acidified with 6 M sulfuric acid. By slow addition of 100 ml ethanol (99 %) to the ice-cooled and stirred solution, orange crystals separated. They were filtered and washed with ethanol (99 %) and acetone. Yield: 1.10 g (83 %). Recrystallization was not necessary. (Found: Co 11.14; C 27.3; N 10.8. Calc. for [Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]HSO<sub>4</sub>·SO<sub>4</sub>·1½H<sub>2</sub>O: Co 11.09; C 27.1; N 10.5.) The hydrogen analyses failed to come out reproducibly. ( $\epsilon, \lambda$ )<sub>max</sub>: (148, 489), (95.9, 353). ( $\epsilon, \lambda$ )<sub>min</sub>: (17.0, 408), (84.6, 334). Half-width: 3453 cm<sup>-1</sup>.

3c.  $\alpha$ -cis-*Diacquabis*(2-picolylamine)cobalt(III) chloride,  $\alpha$ -[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]Cl<sub>3</sub>. 1.70 g  $\alpha$ -[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>3</sub> (3.4 mmol) was dissolved in 10 ml 4 M hydrochloric acid. 2 ml conc. hydrochloric acid was added, and during stirring and ice-cooling the addition of 150 ml ethanol (99 %) resulted in the precipitation of 1.51 g of red-orange crystals. (Yield: 94 % based on [Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>3</sub>, 71 % based on [Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>-Cl<sub>2</sub>]Cl·H<sub>2</sub>O). Washing with acetone. (Found: Co 12.49; C 30.3; N 12.0; H 5.39; Cl 22.8. Calc. for [Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]Cl<sub>3</sub>·3H<sub>2</sub>O: Co 12.50; C 30.6; N 11.9; H 5.56; Cl 22.6.) ( $\epsilon, \lambda$ )<sub>max</sub>: (149, 489), (96.1, 353). ( $\epsilon, \lambda$ )<sub>min</sub>: (17.1, 408), (82.8, 333). Half-width: 3417 cm<sup>-1</sup>.

The same compound could be prepared directly from  $\alpha$ -[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>]Cl·H<sub>2</sub>O, namely by treating this complex with silver oxide and acidifying the filtrate with hydrochloric acid.

1.00 g  $\alpha$ -[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>]Cl·H<sub>2</sub>O (2.5 mmol) was added to moist silver oxide, freshly prepared from 2.4 g silver nitrate (14 mmol). The filtrate was acidified with conc. hydrochloric acid. Precipitation was performed by adding 250 ml ethanol (99 %) during stirring and ice-cooling. Washing as above. Yield 0.81 g (69 %). The absorption spectrum was in complete agreement with that found for  $\alpha$ -[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]Cl<sub>3</sub>·3H<sub>2</sub>O.

4a.  $\alpha$ -cis-*Hydroxoacquabis*(2-picolylamine)cobalt(III) nitrate,  $\alpha$ -[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>OHH<sub>2</sub>O](NO<sub>3</sub>)<sub>2</sub>. 1.10 g  $\alpha$ -[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>3</sub> (2.01 mmol) was dissolved in a mixture of 3 ml water and 1.5 ml pyridine. The slow addition of 100 ml ethanol (99 %) to the red-violet, ice-cooled solution caused the precipitation of a strikingly red compound. Filtration and washing with ethanol and acetone. Yield: 0.71 g (81 %). (Found: Co 13.44; C 33.1; N 19.2; H 4.51. Calc. for [Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>OHH<sub>2</sub>O](NO<sub>3</sub>)<sub>2</sub>: Co 13.57; C 33.2; N 19.4; H 4.41.) ( $\epsilon, \lambda$ )<sub>max</sub>: (126, 504), (79.8, 375). ( $\epsilon, \lambda$ )<sub>min</sub>: (42.2, 430), (59.3, 333). Medium: water. Measured in 0.1 M hydrochloric acid the compound showed an absorption spectrum in agreement with that found for  $\alpha$ -[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>3</sub>.

4b.  $\alpha$ -cis-*Hydroxoacquabis*(2-picolylamine)cobalt(III) chloride,  $\alpha$ -[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>OHH<sub>2</sub>O]Cl<sub>2</sub>. 0.80 g  $\alpha$ -[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]Cl<sub>3</sub>·3H<sub>2</sub>O (1.70 mmol) was dissolved in 4 ml 2 M ammonia. During ice-cooling and stirring, 200 ml ethanol (99 %) was added to precipitate a light-red product. Filtering and washing with ethanol and acetone. Yield: 0.50 g (75 %). (Found: Co 14.91; C 36.6; N 14.2; H 5.13; Cl 18.0. Calc. for [Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>OHH<sub>2</sub>O]Cl<sub>2</sub>·<sup>2</sup>/<sub>3</sub>H<sub>2</sub>O: Co 14.99; C 36.7; N 14.3; H 5.21; Cl 18.0) ( $\epsilon, \lambda$ )<sub>max</sub> (126, 504), (81.4, 375). ( $\epsilon, \lambda$ )<sub>min</sub>: (42.1, 430), (59.4, 332). Medium: water. With 0.1 M hydrochloric acid as a medium, the absorption spectrum showed agreement with the data found for  $\alpha$ -[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]Cl<sub>3</sub>.

5.  $\alpha$ -cis-*Diamminebis*(2-picolylamine)cobalt(III) chloride,  $\alpha$ -[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]Cl<sub>3</sub>. In a conical flask equipped with a drying-tube containing sodium hydroxide pellets, 1.00 g  $\alpha$ -[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>]Cl·H<sub>2</sub>O (2.5 mmol) was covered with approx. 25 ml liquid ammonia. In a few minutes the red compound converted to a yellow one, presumably consisting of [Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]Cl<sub>3</sub>. The flask was left for some hours, and the surplus ammonia was allowed to evaporate. The residue was dissolved in 10 ml 4 M hydrochloric acid. 200 ml ethanol (99 %) was added causing a yellow precipitate to form. Filtration and washing with ethanol; 1.06 g. The recrystallization was performed by dissolving in a few ml boiling 4 M hydrochloric acid, filtering and cooling on ice. Washing as above. To ensure the purity of the final product, the compound was recrystallized twice, although the second recrystallization did not cause any noticeable change of the absorption spectrum, and though the loss of material was appreciable. Yield: 0.51 g (45 %). (Found: Co 13.07; C 31.9; N 18.7; H 5.52; Cl 24.2. Calc. for [Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]Cl<sub>3</sub>·2H<sub>2</sub>O: Co 13.05; C 31.9; N 18.6; H 5.80; Cl 23.6.) The chlorine analysis indicates, that the crystals retain a small amount of hydrochloric acid, which cannot be removed by even careful washing with ethanol. ( $\epsilon, \lambda$ )<sub>max</sub>: (101, 469), (104, 334). ( $\epsilon, \lambda$ )<sub>min</sub>: (11.1, 388), (96.0, 320). Half-width: 3488 cm<sup>-1</sup>.

6.  $\beta$ -cis-*Dinitrobis*(2-picolylamine)cobalt(III) nitrate,  $\beta$ -[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]NO<sub>3</sub>. 5.8 g cobalt(II) nitrate, hexahydrate (20 mmol) and 3.0 g sodium nitrite (43 mmol) were dissolved in 10 ml water. An ice-cooled mixture of 4.3 ml 2-picolylamine (40 mmol) and 1.6 ml conc. nitric acid was added, and the solution was oxidized, a stream of air being drawn through it for 1 h. After cooling on ice, the brown-yellow precipitate was filtered and washed with ice-water and acetone. The crude product was extracted with 180 ml boiling water. The filtrate was cooled on ice and golden platelike crystals separated. Filtering and washing as above. Yield: 4.2 g of presumed  $\beta$ -[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]NO<sub>3</sub>. The addition of lithium bromide to the filtrate gave a lemon-yellow precipitate consisting of the bromide of the  $\alpha$ -form. (Found: Co 11.32; C 27.4; N 16.2; H 4.28; Br 15.6. Calc. for

$[\text{Co}(\text{C}_6\text{H}_5\text{N}_2)_2(\text{NO}_2)_2]\text{Br}\cdot 4\text{H}_2\text{O}$ : Co 11.35; C 27.8; N 16.2; H 4.66; Br 15.4.) ( $\epsilon, \lambda$ )<sub>max</sub>: (295, 439). ( $\epsilon, \lambda$ )<sub>min</sub>: (260, 416). The  $\beta$ -nitrate was recrystallized from 160 ml boiling water. The crystals, which separated from the filtrate by cooling, were filtered and washed as above. Yield: 3.0 g (30 %). (Found: Co 13.72; C 33.3; N 22.7; H 3.74. Calc. for  $[\text{Co}(\text{C}_6\text{H}_5\text{N}_2)_2(\text{NO}_2)_2]\text{NO}_3$ : Co 13.73; C 33.6; N 22.8; H 3.76.) ( $\epsilon, \lambda$ )<sub>max</sub>: (275, 444). ( $\epsilon, \lambda$ )<sub>min</sub>: (148, 402).

7a.  $\beta$ -cis-Dichlorobis(2-picolyamine)cobalt(III) chloride,  $\beta$ - $[\text{Co}(\text{C}_6\text{H}_5\text{N}_2)_2\text{Cl}_2]\text{Cl}$ . 2.15 g  $\beta$ - $[\text{Co}(\text{C}_6\text{H}_5\text{N}_2)_2(\text{NO}_2)_2]\text{NO}_3$  (5.0 mmol) was suspended in a few ml conc. hydrochloric acid. The mixture was heated on a water-bath (100°). A colour-change from yellow-brown via orange to violet took place. The solution was evaporated to dryness. The violet residue, which was washed with acetone and transferred to a glass-filter, was extracted with 20 ml boiling water. To the ice-cold filtrate, 2 g lithium chloride dissolved in 30 ml ethanol was added. Dark-red crystals separated. They were filtered and washed with ethanol and acetone; 1.7 g. The chloride was recrystallized by dissolving in 10 ml boiling water and precipitating the crystals again by the addition of a solution of 2 g lithium chloride in 50 ml ethanol. Washing as above. Yield: 1.4 g (67 %). (Found: Co 14.12; C 34.3; N 13.5; H 4.60; Cl 25.4. Calc. for  $[\text{Co}(\text{C}_6\text{H}_5\text{N}_2)_2\text{Cl}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$ : Co 14.11; C 34.5; N 13.4; H 4.83; Cl 25.5.) ( $\epsilon, \lambda$ )<sub>max</sub>: (113, 534). ( $\epsilon, \lambda$ )<sub>min</sub>: (21.6, 445). Half-width: 3763  $\text{cm}^{-1}$ .

7b.  $\beta$ -cis-Dichlorobis(2-picolyamine)cobalt(III) dithionate,  $\beta$ - $[\text{Co}(\text{C}_6\text{H}_5\text{N}_2)_2\text{Cl}_2]_2\text{S}_2\text{O}_6$ . 1.0 g  $\beta$ - $[\text{Co}(\text{C}_6\text{H}_5\text{N}_2)_2\text{Cl}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$  (2.4 mmol) was dissolved in 15 ml water (70°). A solution of 2.4 g sodium dithionate, dihydrate (10 mmol) in 5 ml water was added. Presumed  $[\text{Co}(\text{C}_6\text{H}_5\text{N}_2)_2\text{Cl}_2]_2\text{S}_2\text{O}_6$  precipitated on cooling. Washing with ice-water and ethanol. The product was recrystallized by dissolving in 80 ml water (70°) and adding a solution of 2.4 g sodium dithionate dihydrate in 10 ml water to the filtrate. Cooling gave a yield of 0.6 g (60 %). (Found: Co 13.84; C 33.6; N 13.3; H 3.75; Cl 16.3. Calc. for  $[\text{Co}(\text{C}_6\text{H}_5\text{N}_2)_2\text{Cl}_2]_2\text{S}_2\text{O}_6$ : Co 13.83; C 33.8; N 13.2; H 3.78; Cl 16.6.) ( $\epsilon/2, \lambda$ )<sub>max</sub>: (112, 534). ( $\epsilon/2, \lambda$ )<sub>min</sub>: (22.2, 450).

8a.  $\beta$ -cis-Diaquabis(2-picolyamine)cobalt(III) hydrogensulfate-sulfate,  $\beta$ - $[\text{Co}(\text{C}_6\text{H}_5\text{N}_2)_2(\text{H}_2\text{O})_2]\text{HSO}_4\cdot\text{SO}_4$ . 0.80 g  $\beta$ - $[\text{Co}(\text{C}_6\text{H}_5\text{N}_2)_2\text{Cl}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$  (1.92 mmol) was added to a hot solution of 1.2 g silver nitrate (7.2 mmol) in 10 ml water. The solution was filtered from the formed silver chloride, and a few drops of conc. nitric acid were added. During ice-cooling and stirring, ethanol and ether were added to precipitate a tar-like oil, presumably consisting of  $\beta$ - $[\text{Co}(\text{C}_6\text{H}_5\text{N}_2)_2(\text{H}_2\text{O})_2](\text{NO}_3)_3\cdot n\text{H}_2\text{O}$ . The liquid was decanted from the sticky residue, which was then dissolved in a few ml 2 M sulfuric acid. To the filtered solution approx. 200 ml ethanol (99 %) was added slowly during stirring and ice-cooling. Red-orange crystals separated. They were filtered, dissolved again in 2 M sulfuric acid and reprecipitated with ethanol. Washing with ethanol. Yield: 0.38 g (36 %). (Found: Co 10.51; C 25.7; N 10.0; H 4.71. Calc. for  $[\text{Co}(\text{C}_6\text{H}_5\text{N}_2)_2(\text{H}_2\text{O})_2]\text{HSO}_4\cdot\text{SO}_4\cdot 3\text{H}_2\text{O}$ : Co 10.55; C 25.8; N 10.0; H 4.87.) ( $\epsilon, \lambda$ )<sub>max</sub>: (106, 489), (95.1, 359). ( $\epsilon, \lambda$ )<sub>min</sub>: (17.7, 412), (91.7, 340). Half-width: 3492  $\text{cm}^{-1}$ .

The same compound was obtainable from the reaction between  $\beta$ - $[\text{Co}(\text{C}_6\text{H}_5\text{N}_2)_2\text{Cl}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$  and silver oxide, the filtrate being acidified with 2 M sulfuric acid. Precipitation with ethanol. The product was recrystallized twice by dissolving in 2 M sulfuric acid and reprecipitating with ethanol (99 %). From 0.70 g  $\beta$ - $[\text{Co}(\text{C}_6\text{H}_5\text{N}_2)_2\text{Cl}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$  (1.68 mmol) a yield of 0.35 g was obtained (37 %). The absorption spectrum was in complete agreement with that found for  $\beta$ - $[\text{Co}(\text{C}_6\text{H}_5\text{N}_2)_2(\text{H}_2\text{O})_2]\text{HSO}_4\cdot\text{SO}_4\cdot 3\text{H}_2\text{O}$ .

8b.  $\beta$ -cis-Diaquabis(2-picolyamine)cobalt(III) bromide,  $\beta$ - $[\text{Co}(\text{C}_6\text{H}_5\text{N}_2)_2(\text{H}_2\text{O})_2]\text{Br}_3$ . 0.50 g  $\beta$ - $[\text{Co}(\text{C}_6\text{H}_5\text{N}_2)_2\text{Cl}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$  (1.2 mmol) was treated with moist silver oxide (from 1.2 g silver nitrate). The filtrate was cooled on ice and acidified with conc. hydrobromic acid. Slowly and during stirring, 350 ml ethanol (99 %) and 50 ml ether were added. The stirring was continued for 1 h. The orange-red precipitate was then filtered and washed with ethanol and ether. Yield: 0.40 g (59 %). (Found: Co 10.46; C 25.5; N 9.91; H 3.67; Br 42.2. Calc. for  $[\text{Co}(\text{C}_6\text{H}_5\text{N}_2)_2(\text{H}_2\text{O})_2]\text{Br}_3\cdot \text{H}_2\text{O}$ : Co 10.36; C 25.3; N 9.85; H 3.90; Br 42.1.) ( $\epsilon, \lambda$ )<sub>max</sub>: (106, 489), (111, 348). ( $\epsilon, \lambda$ )<sub>min</sub>: (18.8, 413). The second minimum was difficult to determine. Half-width: 3443  $\text{cm}^{-1}$ . The position and intensity of the second absorption band compared to the values found for the sulfate-hydrogensulfate seem to indicate, that the bromide is not obtainable in a perfectly pure state. Several recrystallizations did not improve the results. In all cases the bromide tended to come out as a badly crystallizing product.

9.  $\beta$ -cis-Diamminebis(2-picolyamine)cobalt(III) bromide,  $\beta$ - $[\text{Co}(\text{C}_6\text{H}_5\text{N}_2)_2(\text{NH}_3)_2]\text{Br}$ . In a conical flask equipped with a drying-tube containing sodium hydroxide pellets

0.50 g  $\beta$ -[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>]Cl·2H<sub>2</sub>O (1.20 mmol) was covered with approx. 25 ml liquid ammonia. The flask was left for some hours, and the surplus ammonia was allowed to evaporate. The residue was dissolved in 5 ml 4 M hydrochloric acid (yellow-red solution). 2 g lithium bromide was added and afterwards 150 ml ethanol (99 %). A yellow precipitate formed. Filtering and washing with ethanol, 0.56 g. The recrystallization was performed by dissolving in 5 ml 4 M hydrochloric acid, filtering and precipitating with a solution of 2 g lithium bromide in 150 ml ethanol. Washing as above. Yield: 0.42 g (60 %). (Found: Co 10.07; C 24.6; N 14.5; H 4.17; Br 40.8. Calc. for [Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]Br<sub>3</sub>·2H<sub>2</sub>O: Co 10.07, C 24.6, N 14.4; H 4.47; Br 41.0.) ( $\epsilon, \lambda$ )<sub>max</sub>: (105, 466.5), (112, 336). ( $\epsilon, \lambda$ )<sub>min</sub>: (13.0, 388), (95.0, 320). Half-width: 3483 cm<sup>-1</sup>.

### Physical measurements

Electronic absorption spectra were recorded on a Cary Model 14 spectrophotometer. The measurements were made on water solutions at room temperature. <sup>1</sup>H NMR spectra were obtained on a Varian Model A-60 spectrometer using sodium 3-trimethyl-silyl-1-propane ((TPSNa) as an internal standard. In D<sub>2</sub>O the signals arising from the methylene protons were partly overlapped by a band due to water protons (from ligand water, from water of crystallization and from water formed by the fast exchange of protons on the nitrogen atoms). This difficulty was overcome by the addition of CF<sub>3</sub>COOH 20 min after the compound had been dissolved. This caused the water band to move from approx. 4.62 ppm to 5.35 ppm, while the methylene signals remained intact.

### Analyses

The cobalt analyses were performed on a Perkin Elmer 403 Atomic Absorption Spectrophotometer.

The microanalytical laboratory of this institute carried out the carbon, nitrogen, hydrogen, and halogen analyses by standard methods.

## 5. RESULTS AND DISCUSSION

*Characterization of the isomers.* The nitro and chloro complexes of both series crystallize easily and well. The solubilities of corresponding compounds are very alike, but colour variations, which cannot be due only to different crystal-sizes, are noticed (Experimental). The aqua and ammine complexes of both series are very soluble in water, and especially the  $\beta$ -compound tends to crystallize badly and form sticky products, being difficult to purify. The colour-differences are unremarkable.

*Electronic spectra.* The electronic spectra in the visible region of the nine different complex ions are given in Figs. 2–6. A comparison of the long-wavelength bands (Table 1) shows, that the  $\alpha$ -compounds in all cases except for the ammine complex have a greater intensity than the corresponding  $\beta$ -complexes, and that the  $\alpha$ -type bands occur at a higher wavelength in all cases except for the nitro complex. The half-widths of the first band are slightly greater for the  $\beta$ -chloro and aqua complexes (3763 cm<sup>-1</sup>, 3492 cm<sup>-1</sup>) than for the corresponding  $\alpha$ -compounds (3333 cm<sup>-1</sup>, 3453 cm<sup>-1</sup>). This is in agreement with the assumption, that the  $\beta$ -type complexes are less symmetrical than the  $\alpha$ -type. Otherwise it is not possible to deduce anything from the differences. They are, as should be expected, small in any case. The spectrum of  $\alpha$ -*cis*-[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>OHH<sub>2</sub>O](NO<sub>3</sub>)<sub>2</sub> dissolved in 0.1 M hydrochloric acid is in agreement with the spectrum of  $\alpha$ -*cis*-[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>3</sub>, confirming that

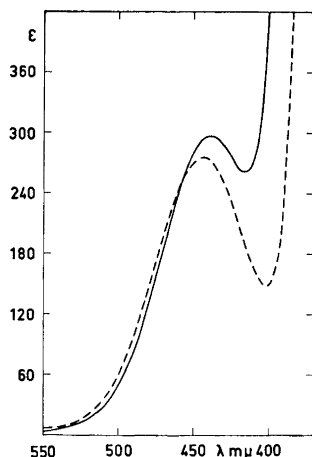


Fig. 2. The absorption spectrum of  $\alpha$ -*cis*- $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2(\text{NO}_2)_2]\text{NO}_2 \cdot \text{H}_2\text{O}$  (—), and of  $\beta$ -*cis*- $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2(\text{NO}_2)_2]\text{NO}_3$  (---). Visible region.

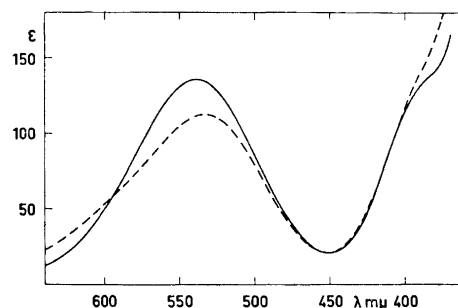


Fig. 3. The absorption spectrum of  $\alpha$ -*cis*- $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$  (—), and of  $\beta$ -*cis*- $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$  (---). Visible region.

the amine configuration is the same in both cases (Table 2). The spectra of  $\alpha$ - and  $\beta$ -*cis*- $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2\text{Cl}_2]\text{Cl}$  in a solution of mercury perchlorate (0.5 M) in perchloric acid (3 M) have been compared to the spectra of  $\alpha$ - and  $\beta$ -*cis*- $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2]\text{HSO}_4 \cdot \text{SO}_4$ , respectively. (The effect of the acid mercury(II) solution is a replacement of the complex-bound chloride (to cobalt) with

Table 1. The wavelengths  $\lambda_{\text{max}}$  and the molar extinction coefficients  $\epsilon_{\text{max}}$  of absorption bands in the visible region for compounds belonging to two different series of *cis*-bis(2-picolylamine) complexes of cobalt(III).

Complex	$\lambda_{\text{max}}\text{nm}$ (1)	$\epsilon_{\text{max}}$ (1)	$\lambda_{\text{max}}\text{nm}$ (2)	$\epsilon_{\text{max}}$ (2)
$\alpha$ - $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2(\text{NO}_2)_2]\text{NO}_2 \cdot \text{H}_2\text{O}$	438.5	296		
$\alpha$ - $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$	538.5	136		
$\alpha$ - $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2]\text{HSO}_4 \cdot \text{SO}_4 \cdot 1\frac{1}{2}\text{H}_2\text{O}$	489	148	353	95.9
$\alpha$ - $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2(\text{NH}_3)_2]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$	469	101	334	104
$\beta$ - $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2(\text{NO}_2)_2]\text{NO}_3$	444	275		
$\beta$ - $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$	534	113		
$\beta$ - $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2]\text{HSO}_4 \cdot \text{SO}_4 \cdot 3\text{H}_2\text{O}$	489	106	353	95
$\beta$ - $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2(\text{NH}_3)_2]\text{Br}_3 \cdot 2\text{H}_2\text{O}$	466.5	105	336	112

water.) The positions and intensities of the long-wavelength bands and the following minima agree (Table 2). The positions of the second bands differ a few nm, and the intensities are slightly higher in the perchloric acid solutions presumably because of an overlap from a charge-transfer band. The spectra of  $\alpha$ - and  $\beta$ -*cis*- $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2]\text{HSO}_4 \cdot \text{SO}_4$  dissolved in a water



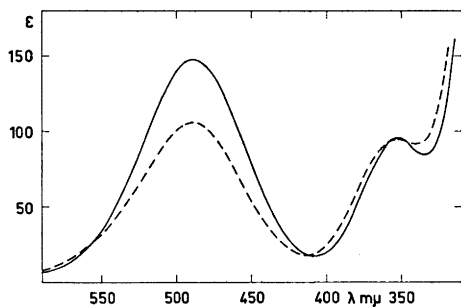


Fig. 4. The absorption spectrum of  $\alpha$ -*cis*- $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2]\text{HSO}_4\cdot\text{SO}_4\cdot 1\frac{1}{2}\text{H}_2\text{O}$  (—), and of  $\beta$ -*cis*- $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2]\text{HSO}_4\cdot\text{SO}_4\cdot 3\text{H}_2\text{O}$  (---). Visible region.

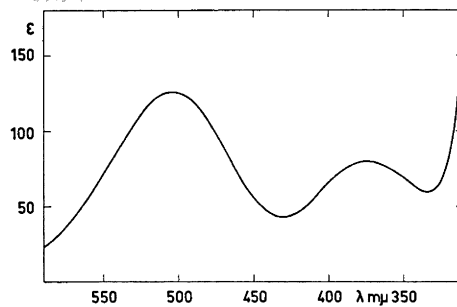


Fig. 5. The absorption spectrum of  $\alpha$ -*cis*- $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2(\text{OH})_2](\text{NO}_3)_2$  (—). Visible region.

solution of sodium nitrite (0.15 M) and left overnight before measuring do not show complete agreement with the spectra of  $\alpha$ - and  $\beta$ -*cis*- $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2(\text{NO}_2)_2]\text{X}$ , although the  $\beta$ -case is very close to. When conc. solutions of  $\alpha$ - and  $\beta$ -*cis*- $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2]\text{HSO}_4\cdot\text{SO}_4$  are boiled for a few minutes with sodium nitrite, and the solutions are cooled in ice, yellow precipitates occur. These products are recrystallized once and are then identified by their absorption spectra as pure  $\alpha$ - and  $\beta$ -*cis*- $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2(\text{NO}_2)_2]\text{NO}_2$ .

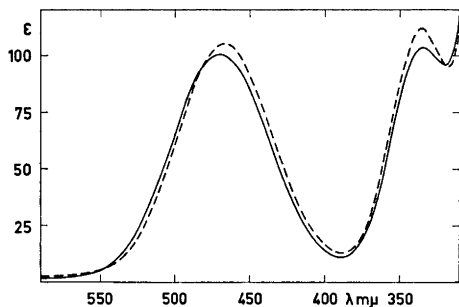


Fig. 6. The absorption spectrum of  $\alpha$ -*cis*- $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2(\text{NH}_3)_2]\text{Cl}_3\cdot 2\text{H}_2\text{O}$  (—), and of  $\beta$ -*cis*- $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2(\text{NH}_3)_2]\text{Br}_3\cdot 2\text{H}_2\text{O}$  (---). Visible region.

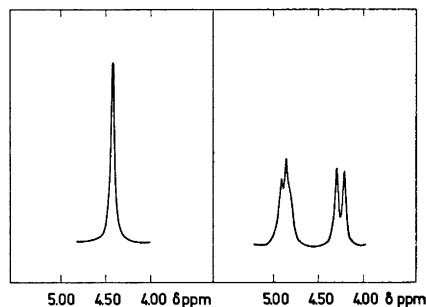


Fig. 7. The methylene proton resonance spectrum of  $\alpha$ -*cis*- $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2]\text{HSO}_4\cdot\text{SO}_4\cdot 1\frac{1}{2}\text{H}_2\text{O}$  (left), and of  $\beta$ -*cis*- $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2]\text{HSO}_4\cdot\text{SO}_4\cdot 3\text{H}_2\text{O}$  (right).

On the basis of these experiments and measurements it should be reasonable to conclude, that the configurations are identical in the  $\alpha$ -chloro,  $\alpha$ -aqua, and  $\alpha$ -nitro complexes and in the  $\beta$ -chloro,  $\beta$ -aqua, and  $\beta$ -nitro complexes, respectively.

*Nuclear magnetic resonance.* Table 3 and Fig. 7 show the  $^1\text{H}$  NMR resonances of the methylene protons in  $\alpha$ - and  $\beta$ -*cis*- $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2]\text{HSO}_4\cdot\text{SO}_4$ .

Table 2. The wavelength  $\lambda_{\max}$  and the molar extinction coefficients  $\epsilon_{\max}$  of the long-wavelength absorption band in the visible region for hydroxo-aqua and aqua complexes measured in other media than pure water.

Complex	Medium	$\lambda_{\max}$ nm	$\epsilon_{\max}$
$\alpha$ -[Co(C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>2</sub> OHH <sub>2</sub> O](NO <sub>3</sub> ) <sub>2</sub>	HCl(0.1 M)	489	147
$\alpha$ -[Co(C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub> ]Cl·H <sub>2</sub> O	Hg <sup>2+</sup> (0.5 M), HClO <sub>4</sub> (3 M)	489	143
$\beta$ -[Co(C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub> ]Cl·2H <sub>2</sub> O	Hg <sup>2+</sup> (0.5 M), HClO <sub>4</sub> (3 M)	489	104

Table 3. Methylene proton chemical shifts.<sup>a</sup>

Complex	Chemical shift $\delta$ ppm	Relative area of peaks
$\alpha$ -[Co(C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]HSO <sub>4</sub> ·SO <sub>4</sub> ·1½H <sub>2</sub> O	4.42	
$\alpha$ -[Co(C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]Cl <sub>3</sub> ·2H <sub>2</sub> O	4.50	
$\beta$ -[Co(C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]HSO <sub>4</sub> ·SO <sub>4</sub> ·3H <sub>2</sub> O	4.22, 4.30, 4.85	1 : 1 : 2
$\beta$ -[Co(C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]Br <sub>3</sub> ·2H <sub>2</sub> O	4.28, 4.43, 4.72	1 : 1 : 2

<sup>a</sup> Measured from TPSNa as an internal standard. All compounds were dissolved in D<sub>2</sub>O. CF<sub>3</sub>COOH was added after 20 min, and the spectra were run.

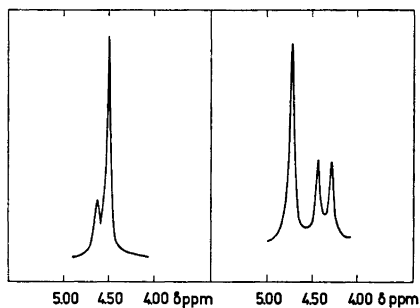
The complicated spectrum of the  $\beta$ -compound (right) compared to the simple  $\alpha$ -spectrum (left), immediately causes one to assign the *cis, cis, cis* configuration to the  $\beta$ -compound, the more symmetrical *cis, trans, cis* or *cis, cis, trans* configuration to the  $\alpha$ -compound.

A *cis, trans, cis* and a *cis, cis, trans* isomer (Fig. 1a and b) both possess a C<sub>2</sub> axis. The corresponding atoms on the two ligands are consequently related by symmetry. Thus one resonance signal is expected for each kind of protons on the ligand. In this case we have two different methylene protons and therefore expect to observe two singlets.  $\alpha$ -*cis*-[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]HSO<sub>4</sub>·SO<sub>4</sub> shows a spectrum consisting of one band, which is apparently a sum of two singlets (the area of the peak is the half of the total area of the peaks of the pyridine protons), thus confirming our assumptions.

A *cis, cis, cis* isomer is totally asymmetric (Fig. 1c), and two resonance signals are expected for each kind of methylene protons. We should therefore expect four singlets. We observe in the  $\beta$ -case three bands, two close singlets and a broad band, which is apparently a sum of two singlets (the total area of the methylene peaks is the half of the total area of the peaks of the pyridine protons). This is in agreement with the expected lack of symmetry for a *cis, cis, cis* isomer.

Table 3 and Fig. 8 show the <sup>1</sup>H NMR resonances of the methylene protons in  $\alpha$ - and  $\beta$ -*cis*-[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]X<sub>3</sub>. Both spectra bear a resemblance to the spectra of the corresponding aqua complexes, thus suggesting a common amine configuration in the  $\alpha$ - and in the  $\beta$ -cases, respectively.

Fig. 8. The methylene proton resonance spectrum of  $\alpha$ -*cis*-[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]-Cl<sub>3</sub>·2H<sub>2</sub>O (left), and of  $\beta$ -*cis*-[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]-Br<sub>3</sub>·2H<sub>2</sub>O (right).



The  $\alpha$ -spectrum (left) shows one band, evidently the sum of two singlets (the area of the peak is the half of the area of the peaks of the pyridine protons). The small band at 4.63 ppm is perhaps due to nitrogen-bound protons, which in this special case have not been exchanged.  $\alpha$ -*cis*-[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]-X<sub>3</sub>, when dissolved in an acid solution of D<sub>2</sub>O, shows a spectrum with a broad band (4.50–4.67 ppm), which is presumed to originate from nitrogen-bound protons (they have not been exchanged with D<sup>+</sup> in this acid solution<sup>11</sup>). This product (see Experimental) is perhaps contaminated with a small amount of hydrochloric acid, which could be responsible for the incomplete deuteration of the nitrogen-bound protons.

The  $\beta$ -spectrum (right) again shows two close singlets and a high intensity band, which is probably a sum of two singlets.

Fig. 9 shows the <sup>1</sup>H NMR resonances of the pyridine protons in  $\alpha$ - and  $\beta$ -*cis*-[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]-HSO<sub>4</sub>·SO<sub>4</sub>. As should be expected the  $\beta$ -spectrum (bottom) is more complicated than the  $\alpha$ -spectrum (top).

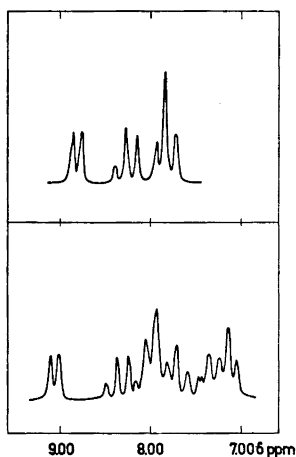


Fig. 9. The pyridine proton resonance spectrum of  $\alpha$ -*cis*-[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]-HSO<sub>4</sub>·SO<sub>4</sub>·1½H<sub>2</sub>O (top), and of  $\beta$ -*cis*-[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]-HSO<sub>4</sub>·SO<sub>4</sub>·3H<sub>2</sub>O (bottom).

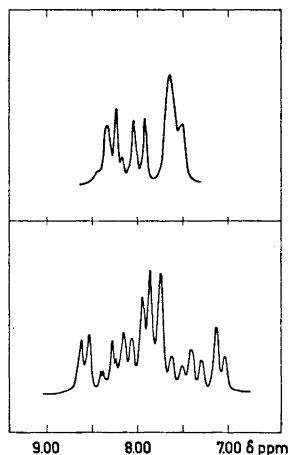


Fig. 10. The pyridine proton resonance spectrum of  $\alpha$ -*cis*-[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]-Cl<sub>3</sub>·2H<sub>2</sub>O (top), and of  $\beta$ -*cis*-[Co(C<sub>6</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]-Br<sub>3</sub>·2H<sub>2</sub>O (bottom).

Fig. 10 shows the  $^1\text{H}$  NMR resonances of the pyridine protons in  $\alpha$ - and  $\beta$ -*cis*- $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2(\text{NH}_3)_2]\text{X}_3$ . The resemblance to the spectra of the corresponding aqua complexes again confirms the common amine configuration through the series.

Thus the  $^1\text{H}$  NMR spectra strongly indicate, that  $\alpha$ -*cis*- $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2]\text{HSO}_4\cdot\text{SO}_4$  and  $\alpha$ -*cis*- $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2(\text{NH}_3)_2]\text{X}_3$  have the same configuration, namely a *cis, trans, cis* or a *cis, cis, trans*, and that  $\beta$ -*cis*- $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2]\text{HSO}_4\cdot\text{SO}_4$  and  $\beta$ -*cis*- $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2(\text{NH}_3)_2]\text{X}_3$  have the same configuration, namely a *cis, cis, cis*.

Due to the relatively low solubilities of the nitro and chloro complexes in  $\text{D}_2\text{O}$ , the  $^1\text{H}$  NMR spectra of most of these compounds were rather useless. However  $\alpha$ -*cis*- $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2\text{Cl}_2]\text{Cl}$  could be measured with some advantage. The spectrum of the methylene protons showed two very close singlets (areas 1 : 1), and the spectrum of the pyridine protons showed the same characteristic traits as those found for  $\alpha$ -*cis*- $[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2]\text{HSO}_4\cdot\text{SO}_4$ .

*Conclusion.* The absorption spectra and the  $^1\text{H}$  NMR spectra in combination make it reasonable to assume, that all complexes belonging to the  $\beta$ -series have the same configuration, namely a *cis, cis, cis* (Fig. 1c), and that all complexes belonging to the  $\alpha$ -series have the same configuration, namely a *cis, trans, cis* or a *cis, cis, trans* (Fig. 1a or b). We hope before long to be able to decide, whether in the last case the pyridine-nitrogens or the methylamine-nitrogens are in the *trans* positions to each other.

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