

A Double-bridged Binuclear Chromium(III) Complex with 1,6-Bis(2'-pyridyl)-2,5-diazahexane. Preparation, Resolution and Stereochemistry of the Di- μ -hydroxobis[1,6-bis(2'-pyridyl)-2,5-diazahexane]chromium(III) Ion

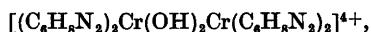
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A new binuclear chromium(III) complex of the double-bridged type $[(C_{14}H_{18}N_4)Cr(OH)_2Cr(C_{14}H_{18}N_4)]^{4+}$, where the tetramine ligand $C_{14}H_{18}N_4 = 1,6$ -bis(2'-pyridyl)-2,5-diazahexane (N,N' -bis-(2-methylpyridyl)-1,2-ethanediamine, abbrev. bispicen), has been prepared and resolved into its catoptric forms. As this di- μ -hydroxo complex reacts with hydrochloric acid to α -*cis*- $[Cr(C_{14}H_{18}N_4)Cl_2]^+$, this type of compounds was included in the study. Both the symmetrical α -*cis* and the unsymmetrical β -*cis*-dichloro complex were prepared for the first time and compared with the earlier described cobalt(III) complexes of the same types. The stereochemistry of the complexes was deduced from electronic spectra, CD-spectra, 1H NMR spectra and X-ray powder photographs.

Binuclear chromium(III) complexes with two hydroxo groups as bridging ligands, the so-called diols, have recently attracted much attention because of their kinetic,^{1,2} spectroscopic,³⁻⁶ structural and magnetic properties.⁷⁻¹⁰

In a previous work by the present author,¹¹ the synthesis, resolution and properties of the binuclear ion



where the bidentate ligand $C_6H_5N_2 = 2$ -aminomethylpyridine, were reported. This work concerns di- μ -hydroxo- and *cis*-dichloro complexes of chromium(III) with the related tetradentate ligand $C_{14}H_{18}N_4 = 1,6$ -bis(2'-

pyridyl)-2,5-diazahexane (N,N' -bis(2-methylpyridyl)-1,2-ethanediamine, abbrev. bispicen), Fig. 1.

Gibson and McKenzie¹² prepared both the symmetrical α -*cis* and the unsymmetrical β -*cis*-dichloro complexes of cobalt(III) and bispicen and based the structural assignment of the isomers on PMR-spectra. As X-ray powder photographs showed isomorphism between these compounds and the new *cis*-dichloro complexes of chromium(III), an assignment of the configuration of the latter was possible.

EXPERIMENTAL

Reagents. Pyridine-2-carboxaldehyde was purchased from Merck-Schuchardt. *trans*- $[Crpy_4Cl_2]I$ and *trans*- $[CoPy_4Cl_2]Cl \cdot 6H_2O$ were prepared by methods developed by Glerup and Schäffer¹³ and Werner and Feenstra,¹⁴ respectively. All other chemicals were of chemical grade and were used without further purification.

Analyses. The chromium and cobalt analyses were performed on a Perkin Elmer 403 Atomic Absorption Spectrophotometer. The micro-analytical laboratory of this institute carried out the carbon, nitrogen, hydrogen and halogen analyses by standard methods.

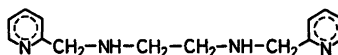


Fig. 1. 1,6-Bis(2'-pyridyl)-2,5-diazahexane, $C_{14}H_{18}N_4$.

Physical measurements. Absorption spectra were recorded on a Cary Model 14 spectrophotometer. The spectra are characterized by their maxima and minima (ϵ, λ), where the molar extinction coefficient ϵ is in units of $l \text{ mol}^{-1} \text{ cm}^{-1}$ and λ is in nm. Circular dichroism was measured on a Roussel-Jouan Dicrographe I. The maxima are given below as $(\Delta\epsilon, \lambda) = [(\epsilon_1 - \epsilon_2), \lambda]$. Optical rotation was measured on a Perkin Elmer Model 141 polarimeter. In all cases the solvent was 0.1 M hydrochloric acid. The X-ray powder photographs were obtained on a camera of the Guinier type with $\text{CuK}\alpha$ radiation. Silicon was used as standard. ^1H NMR spectra were obtained on a Varian Model A-60 spectrometer using $(\text{CD}_3)_2\text{SO}$ as solvent and tetramethylsilane as standard.

Preparations

1. 1,6-Bis(2'-pyridyl)-2,5-diazahehexane (abbrev. bispicen), $\text{C}_{14}\text{H}_{18}\text{N}_4$. The ligand was prepared from pyridine-2-carboxaldehyde (79 g ~ 0.74 mol) and 1,2-ethanediamine (15 g, 0.25 mol) following mainly the method described by Goodwin and Lions,¹⁵ but with the modification that the crude amine was purified before the final distillation. The purification (via the hydrochloride) was performed as follows: The crude amine was dissolved in the fivefold amount of ethanol (99 %); the solution was cooled on ice, and the hydrochloride was precipitated by the addition of conc. hydrochloric acid. Filtering and washing with ethanol. 41 g. The compound was recrystallized by dissolving in 4 M hydrochloric acid (100 ml) and adding of ethanol (600 ml, 99 %). Yield: 31 g (29 %). Anal. $\text{C}_{14}\text{H}_{18}\text{N}_4 \cdot 4\text{HCl} \cdot 2\text{H}_2\text{O}$: C, N, H, Cl. From the pure hydrochloride the amine was liberated with base and isolated and distilled as described before.¹⁵ Yield: ~ 10 g (16–17 %).

2a. α -cis-Dichloro{1,6-bis(2'-pyridyl)-2,5-diazahehexane}cobalt(III) chloride, α -cis- $[\text{Co}(\text{C}_{14}\text{H}_{18}\text{N}_4)\text{Cl}_2]\text{Cl} \cdot 1.33 \text{ H}_2\text{O}$. 4.00 g *trans*- $[\text{Co}(\text{C}_{14}\text{H}_{18}\text{N}_4)\text{Cl}_2]\text{Cl} \cdot 6\text{H}_2\text{O}$ (6.78 mmol) was dissolved in pyridine (80 ml). Heating and stirring. 2.0 ml of bispicen (> 7 mmol) were added dropwise, and a violet precipitate soon appeared. Cooling, filtering and washing with pyridine and acetone. The crude product was dissolved in the necessary amount of hot (80 °C) 4 M hydrochloric acid (10–12 ml). After filtering and cooling of the filtrate on ice, ethanol (500 ml, 99 %) and ether (10 ml) were added to precipitate 2.01 g of blue-violet crystals (69 %). The crystals were recrystallized again with a loss of 10 %. Anal. $[\text{Co}(\text{C}_{14}\text{H}_{18}\text{N}_4)\text{Cl}_2]\text{Cl} \cdot 1.33 \text{ H}_2\text{O}$: Co, C, N, H, Cl. The content of crystal-water was confirmed by thermogravimetry. (ϵ, λ)_{max}: (128, 541.5), (131, 392.5). (ϵ, λ)_{min}: (19, 454), (129, 382). Half-width δ : 3789 cm^{-1} (1. band).

2b. The perchlorate, α -cis- $[\text{Co}(\text{C}_{14}\text{H}_{18}\text{N}_4)\text{Cl}_2]\text{ClO}_4$, was prepared from the chloride (0.60 g 1.39 mmol) by dissolving in 0.1 M hydrochloric acid (6 ml) and adding 2 ml of a 1 M solution of sodium perchlorate. Cooling on ice and filtering. Washing with icewater. Yield: 0.57 g (86 %). Anal. $[\text{Co}(\text{C}_{14}\text{H}_{18}\text{N}_4)\text{Cl}_2]\text{ClO}_4$: Co, C, N, H, Cl. (ϵ, λ)_{max}: (128, 541.5), (132, 392). (ϵ, λ)_{min}: (19, 454), (130, 382).

3. β -cis-Dinitro{1,6-bis(2'-pyridyl)-2,5-diazahehexane}cobalt(III) nitrate, β -cis- $[\text{Co}(\text{C}_{14}\text{H}_{18}\text{N}_4)(\text{NO}_2)_2]\text{NO}_3 \cdot \text{H}_2\text{O}$. The principle in the method, aerial oxidation of Co(II) in the presence of amine and sodium nitrite, was taken from Holtzclaw *et al.*,¹⁶ and was earlier used by the author in the preparation of a similar compound.¹⁷ 4.24 g bispic. $4\text{HCl} \cdot 2\text{H}_2\text{O}$ (10 mmol) was dissolved in 15 ml 2 M sodium hydroxide (30 mmol). Cobalt nitrate, hexahydrate (2.91 g, 10 mmol) and sodium nitrite (1.40 g, 20 mmol) were added, and the solution was oxidized, air being drawn through it for 3 h. Cooling on ice, filtering and washing with ice-water. The yellow compound was recrystallized from boiling water. Washing as above. Yield: 1.3 g (28 %). Anal. $[\text{Co}(\text{C}_{14}\text{H}_{18}\text{N}_4)(\text{NO}_2)_2]\text{NO}_3 \cdot \text{H}_2\text{O}$: Co, C, N, H. (ϵ, λ)_{max}: (334, 446). (ϵ, λ)_{min}: (196, 405).

The mother liquor and all the filtrates from washings and recrystallizations were kept and used for the preparation of β -cis- $[\text{Co}(\text{C}_{14}\text{H}_{18}\text{N}_4)\text{Cl}_2]\text{NO}_3$ (4a).

4a. β -cis-Dichloro{1,6-bis(2'-pyridyl)-2,5-diazahehexane}cobalt(III) nitrate, β -cis- $[\text{Co}(\text{C}_{14}\text{H}_{18}\text{N}_4)\text{Cl}_2]\text{NO}_3 \cdot \frac{1}{2} \text{H}_2\text{O}$. Solid lithium chloride (~ 10 g) was added to the mixed filtrates from the preparation of 3. After 3 days a brick-red precipitate, presumably $[\text{Co}(\text{C}_{14}\text{H}_{18}\text{N}_4)\text{Cl}(\text{NO}_2)]\text{Cl}$ was filtered. Washing with ethanol. Yield: 2.2 g. A slurry of this compound and conc. hydrochloric acid (15 ml) was evaporated to nearly dryness on a boiling water-bath. Cooling on ice and washing on a filter with acetone. The new crude product was dissolved in 1 M hydrochloric acid (15 ml, 35 °C, a few ml of conc. nitric acid was added, and a red compound precipitated. Yield: 1.90 g (43 % based on $\text{Co}(\text{NO}_2)_2 \cdot 6\text{H}_2\text{O}$). Anal. $[\text{Co}(\text{C}_{14}\text{H}_{18}\text{N}_4)\text{Cl}_2]\text{NO}_3 \cdot \frac{1}{2} \text{H}_2\text{O}$: Co, C, N, H, Cl. The content of crystal-water was found by thermogravimetry to be 0.45. (ϵ, λ)_{max}: (158, 532). (ϵ, λ)_{min}: (35, 454.5). Half-width δ : 3278 cm^{-1} .

4b. The dithionate, β -cis- $[\text{Co}(\text{C}_{14}\text{H}_{18}\text{N}_4)\text{Cl}_2]_2 \cdot \text{S}_2\text{O}_8 \cdot 1\frac{1}{2} \text{H}_2\text{O}$, was prepared from the nitrate (0.20 g, 0.45 mmol) by dissolving in water (25 ml) and adding a saturated solution of sodium dithionate, dihydrate (0.20 g). Cooling on ice. The red precipitate was filtered and washed with ice-water and ethanol. Yield: 0.088 g (42 %). Anal. $[\text{Co}(\text{C}_{14}\text{H}_{18}\text{N}_4)\text{Cl}_2]_2 \cdot \text{S}_2\text{O}_8 \cdot 1\frac{1}{2} \text{H}_2\text{O}$: Co, C, N, H, Cl. The content of crystal-water was found by thermogravimetry to be 1.40. In other experiments the compound crystallized with different contents of crystal-water (for instance 2.50). ($\epsilon/2, \lambda$)_{max}: (158, 532). ($\epsilon/2, \lambda$)_{min}: (37, 452.5).

5a. α -*cis*-Dichloro{1,6-bis(2'-pyridyl)-2,5-diazahexane}chromium(III) chloride, α -*cis*-[Cr(C₁₄H₁₈N₄)Cl₂]Cl₃·3H₂O. 1.60 g anhydrous chromium(III) chloride (10 mmol) was suspended in 20 ml dimethyl sulfoxide. During heating and stirring bispicen (2.0 ml ~ 10 mmol) was added slowly causing a violet solid to form. Cooling and filtering. The solid was washed with ethanol and extracted with 1 M hydrochloric acid (35 ml, 90°C). Cooling of the filtrate on ice gave needle-shaped blue-violet crystals, which were washed as above. Yield: 0.97 g of a practically pure product (21%). By a repeated recrystallization 50% of the material was lost. Anal. [Cr(C₁₄H₁₈N₄)Cl₂]Cl₃·3H₂O: Cr, C, N, H, Cl. The content of crystal-water was checked by thermogravimetry. (ϵ, λ)_{max}: (104, 545), (99, 407.5). (ϵ, λ)_{min}: (25, 464), (5, 354). Halfwidth δ : 3334 cm⁻¹. The mother liquor was kept and used for the isolation of β -*cis*-[Cr(C₁₄H₁₈N₄)Cl₂]Cl.

5b. The perchlorate, α -*cis*-[Cr(C₁₄H₁₈N₄)Cl₂]ClO₄, was prepared from the chloride (0.25 g, 0.55 mmol) by dissolving in about 20 ml water (40°C) and adding 1 M sodium perchlorate solution (5 ml). Cooling on ice and filtering. Washing with ice-water. Yield: 0.21 g (82%). Anal. [Cr(C₁₄H₁₈N₄)Cl₂]ClO₄: Cr, C, N, H, Cl. (ϵ, λ)_{max}: (105, 545), (101, 407.5). (ϵ, λ)_{min}: (27, 464), (11, 354).

6a. β -*cis*-Dichloro{1,6-bis(2'-pyridyl)-2,5-diazahexane}chromium(III) nitrate, β -*cis*-[Cr(C₁₄H₁₈N₄)Cl₂]NO₃· $\frac{3}{2}$ H₂O. The mother liquor from the synthesis of the corresponding α -compound (see 5a) was cooled on ice, and ether was added to precipitate a sticky product. This was dissolved in ethanol and reprecipitated with ether. Finally the product was dissolved in water (12 ml, slightly acid, 42°C), and conc. nitric acid was added to the filtrate precipitating a red crystalline nitrate. Washing with ethanol. Yield: 0.20 g (4.5%). Anal. [Cr(C₁₄H₁₈N₄)Cl₂]NO₃· $\frac{3}{2}$ H₂O: Cr, C, N, H, Cl. The content of crystal-water was confirmed by thermogravimetry. (ϵ, λ)_{max}: (131, 538), (100, 407). (ϵ, λ)_{min}: (47, 464.5), (13, 354). Halfwidth, δ : 3698 cm⁻¹.

6b. The dithionate, β -*cis*-[Cr(C₁₄H₁₈N₄)Cl₂]₂S₂O₈·2H₂O, could be prepared from the nitrate and sodium dithionate, but was also obtained by an alternative method. 2.50 g *trans*-[Crpy₂Cl₂]I (4.42 mmol) was suspended in 10–15 ml 2-methoxyethanol. While heating and stirring bispicen (1.0 ml, ~4.4 mmol) was added. After a period of complete dissolution a dark-violet solid (presumably a mixture of α - and β -[Cr(C₁₄H₁₈N₄)Cl₂]I) precipitated. Cooling on ice, filtering and washing with ethanol. 1.15 g. The crude product was treated with freshly prepared silver chloride, and finely pulverized sodium dithionate, dihydrate (0.5 g) was added to the filtrate (~10 ml). Cooling on ice, filtering and washing with ice-water and ethanol. Yield: 0.26 g (13%). Anal. [Cr(C₁₄H₁₈N₄)Cl₂]₂S₂O₈.

2H₂O: Cr, C, N, H, Cl. By thermogravimetry the content of crystal water was found to be 1.85. (ϵ, λ)_{max}: (134, 538), (101, 407). (ϵ, λ)_{min}: (47, 464.5), (19, 355).

7. Di- μ -hydroxobis[{1,6-bis(2'-pyridyl)-2,5-diazahexane}chromium(III)]iodide, [(C₁₄H₁₈N₄)Cr(OH)₂Cr(C₁₄H₁₈N₄)]I₂·3H₂O. 1.00 g [CrBr₂(H₂O)₄]Br·2H₂O (2.50 mmol) was dissolved in 8–10 ml 2-methoxyethanol, and a spatula of zinc powder and 1.0 ml bispicen (~4.4 mmol) were stirred in. A red precipitate was filtered after 10 min. Washing with 2-methoxyethanol. The crude product was dissolved in boiling water (~15 ml), and sodium iodide (2 g) and ethanol (15 ml, 99%) were added. Cooling on ice. Filtering and washing with ethanol. Yield: 1.36 g (92%). The practically pure compound was recrystallized from boiling water (15 ml) to give 0.91 g shining, flaky crystals directly and 0.41 g further by addition of sodium iodide (1 g) to the filtrate. Anal. [Cr(C₁₄H₁₈N₄)(OH)₂]₂I₂·3H₂O: Cr, C, N, H, I. (ϵ, λ)_{max}: (197, 534), (150, 385). (ϵ, λ)_{min}: (35, 437), (84, 350).

8a. (-)_D-Di- μ -hydroxobis[{1,6-bis(2'-pyridyl)-2,5-diazahexane}chromium(III)]diantimonyl (+)_D-tartrate diiodide, (-)_D-[(C₁₄H₁₈N₄)Cr(OH)₂Cr(C₁₄H₁₈N₄)]{(+)_D-SbOC₄H₄O₆]₂I₂·11H₂O. [Cr(C₁₄H₁₈N₄)(OH)₂]₂I₂·3H₂O (1.78 g, 1.50 mmol) was dissolved in 20 ml hot water (70°C). Sodium antimonyl (+)_D-tartrate (1.88 g, 6.09 mmol) was dissolved in 10 ml hot water (70°C). The solutions were mixed, gently heated for a moment and then cooled on ice for an hour. By then shining, red crystals had deposited. Filtering and washing, first with a mixture of ethanol and water (50%), finally with ethanol (99%). The compound was recrystallized from boiling water (10 ml). Yield: 1.15 g (47%). Anal. [Cr(C₁₄H₁₈N₄)(OH)₂]₂(SbOC₄H₄O₆)₂I₂·11H₂O: Cr, C, N, H, I. In other experiments the complex crystallized with 6, 7, or 12 mol of crystal-water. (ϵ, λ)_{max}: (196, 534), (151, 385). (ϵ, λ)_{min}: (35, 437), (80, 350). ($\Delta\epsilon, \lambda$)_{max}: (-5.35, 520), (+0.48, 443) (+1.16, 382). The mother liquor was kept and used for the isolation of the (+)_D-form.

8b. (+)_D-Di- μ -hydroxobis[{1,6-bis(2'-pyridyl)-2,5-diazahexane}chromium(III)]antimonyl (+)_D-tartrate, (+)_D-[(C₁₄H₁₈N₄)Cr(OH)₂Cr(C₁₄H₁₈N₄)]{(+)_D-SbOC₄H₄O₆]₂·14H₂O. Ethanol (99%) was added to the mother liquor from 8a to double the volume. The resulting fine precipitate was filtered and washed with a mixture of ethanol and water (50%) and with ethanol (99%). Recrystallization from boiling water (8–9 ml) gave fine, violet crystals, which were washed as above. Yield: 1.12 g (37%). Anal. [Cr(C₁₄H₁₈N₄)(OH)₂]₂(SbOC₄H₄O₆)₂·12H₂O: Cr, C, N, H. (ϵ, λ)_{max}: (196, 534), (151, 385). (ϵ, λ)_{min}: (36, 437), (82, 350). ($\Delta\epsilon, \lambda$)_{max}: (+5.32, 520), (-0.48, 443), (-1.15, 383).

9a. (-)_D-Di- μ -hydroxobis[{1,6-bis(2'-pyridyl)-2,5-diazahexane}chromium(III)]iodide, (-)_D-[(C₁₄H₁₈N₄)Cr(OH)₂Cr(C₁₄H₁₈N₄)]I₂·3H₂O.

(-)_D-[Cr(C₁₄H₁₈N₄)(OH)]₂(+)_D-SbOC₄H₄O₆·I₂·11H₂O (0.83 g, 0.50 mmol) was dissolved in 1 M sodium hydroxide solution (4 ml). Ethanol (100 ml, 99 %) was added dropwise while stirring and cooling to precipitate sodium antimonyl (+)_D-tartrate. Filtering. Then 4 M hydrochloric acid was added to recreate the originally red-violet colour of the diol, and at last sodium iodide (3 g) and a small amount of ascorbic acid were added to precipitate the optically active diol as an iodide. Recrystallization from boiling water (5 ml) with the addition of sodium iodide (1 g) to the filtrate. Washing with ethanol. Yield: 0.447 g (75 %). Anal. [Cr(C₁₄H₁₈N₄)(OH)]₂I₂·3H₂O: Cr, C, N, H, I. (ε, λ)_{max}: (195, 534), (147, 385). (ε, λ)_{min}: (35, 437), (82, 350). (Δε, λ)_{max}: (-5.30, 520), (+0.43, 443), (+1.10, 382).

9b. (+)_D-Di-μ-hydroxobis[1,6-bis-(2'-pyridyl)-2,5-diazaheptane]chromium(III) perchlorate, (+)_D-[Cr(C₁₄H₁₈N₄)₂(OH)₂Cr(C₁₄H₁₈N₄)₂](ClO₄)₄·4H₂O.

(+)_D-[Cr(C₁₄H₁₈N₄)(OH)]₂(+)_D-SbOC₄H₄O₆·1.14H₂O was dissolved in hot water (8 ml, 70 °C). Sodium perchlorate (1 g) dissolved in water (1 ml) was added. A fluffy precipitate, presumed to be a mixed perchlorate-antimonyl tartrate, immediately appeared. Filtering and washing with ice-water. The compound was dissolved on the filter in boiling water (25 ml). Sodium perchlorate (5 g) was added, and coarse well-shaped crystals appeared on cooling. Recrystallization from boiling water (10 ml) with the addition of sodium perchlorate (1 g) dissolved in water (1 ml). Cooling. Filtering. Washing with ethanol. Yield: 0.197 g (72 %). Anal. [Cr(C₁₄H₁₈N₄)(OH)]₂(ClO₄)₄·4H₂O: Cr, C, N, H, Cl. (ε, λ)_{max}: (197, 534), (150, 385). (ε, λ)_{min}: (36, 437), (78, 350). (Δε, λ)_{max}: (+5.42, 520), (-0.47, 443), (-1.13, 383).

10. (+)_D-α-cis-Dichloro[1,6-bis-(2'-pyridyl)-diazaheptane]chromium(III) perchlorate, (+)_D-α-cis-[Cr(C₁₄H₁₈N₄)Cl₂ClO₄].

(+)_D-[Cr(C₁₄H₁₈N₄)(OH)]₂(ClO₄)₄·4H₂O (0.245 g, 0.224 mmol) was kept in a stoppered flask with conc. hydrochloric acid (2 ml) for 4 days. By then large violet crystals had formed. They were filtered and washed, first with 1 M sodium perchlorate solution, then with ethanol. Yield: 0.147 g (71 %). (ε, λ)_{max}: (103, 545), (98, 407). (ε, λ)_{min}: (26, 464), (8, 353). (Δε, λ)_{max}: (-1.06, 583), (+1.10, 511), (-0.12, 395).

RESULTS AND DISCUSSION

Synthesis and resolution. Gibson and McKenzie¹² synthesized α-cis-[Co(C₁₄H₁₈N₄)Cl₂]⁺ using the so-called sodium triscarbonatocobaltate(III) as an initial material. We developed another method starting from (trans-[C₁₀py₄Cl₂]Cl₂·6H₂O), which reacted with the amine in an organic medium. β-cis-[Co(C₁₄H₁₈N₄)Cl₂]⁺ was evidently prepared by the same conventional method

in both cases,^{12,16-18} namely by an oxidation with air of the cobalt(II) ion in the presence of amine and sodium nitrite and a subsequent substitution of the nitro groups in the β-cis-dinitro complex formed.

Anhydrous chromium(III) chloride and trans-[C₁₀py₄Cl₂]I react with 2-aminomethylpyridine forming α- and β-cis-[Cr(C₁₄H₁₈N₄)₂Cl₂]⁺, respectively.¹⁹ In the case of 1,6-bis-(2'-pyridyl)-2,5-diazaheptane the same starting materials both gave mixtures of the α- and β-compounds. Differences in solubilities enabled us to separate the compounds, but the final yields were accordingly small.

We have earlier found¹¹ that the di-μ-hydroxobis[bis(2-aminomethylpyridine)chromium(III)] ion could be obtained by the reaction of chromium(III) bromide, hexahydrate and 2-aminomethylpyridine in the presence of chromium(II) or zinc dust. In the present case the method worked equally well, zinc dust being preferred because it was more easily available.

Like the corresponding diols with 2-aminomethylpyridine, 1,10-phenanthroline and 2,2'-bipyridine, the diol with 1,6-bis-(2'-pyridyl)-2,5-diazaheptane could be resolved with sodium antimonyl (+)_D-tartrate as a resolving agent.^{11,5} In all cases the (-)_D-isomer formed the less soluble diastereoisomer. The reaction between the perchlorate of the (+)_D-isomer and conc. hydrochloric acid gave (+)_D-[Cr(C₁₄H₁₈N₄)Cl₂]ClO₄, identified as belonging to the α-type of cis-complexes by means of the absorption spectrum.

Stereochemistry of the cis-dichloro 1,6-bis-(2'-pyridyl)-2,5-diazaheptane-chromium(III) ions. The general formula cis-[M(C₁₄H₁₈N₄)Cl₂]⁺, where M is Co(III) or Cr(III) and C₁₄H₁₈N₄ = 1,6-bis-(2'-pyridyl)-2,5-diazaheptane, theoretically includes two types of geometrical isomers, namely isomers with the symmetrical α-cis configuration (Fig. 2a, b) and isomers with the

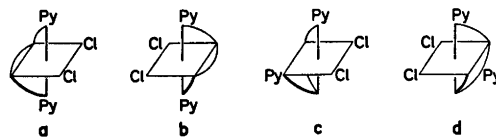


Fig. 2. α- and β-cis-[M(C₁₄H₁₈N₄)Cl₂]⁺. M = Cr(III) or Co(III). Py symbolizes the pyridine nitrogen. a, A (α). b, A' (α). c, A (β). d, A' (β).

Table 1. Data from X-ray powder photographs.

Compound	<i>d</i> -Spacings (Å)
α - <i>cis</i> -[Co(C ₁₄ H ₁₈ N ₄)Cl ₂]ClO ₄	8.98 m, 7.61 s, 7.19 s, 6.69 w, 6.39 s, 5.66 s, 5.62 m, 5.53 m, 5.23 s, 5.08 w, 4.87 s, 4.60 w, 4.40 w, 4.36 w, 4.28 m, 4.23 m, 3.86 m, 3.79 m, 3.69 m, 3.63 s, 3.57 m, 3.49 m, 3.35 w, 3.33 s.
α - <i>cis</i> -[Cr(C ₁₄ H ₁₈ N ₄)Cl ₂]ClO ₄	9.03 m, 7.65 s, 7.19 s, 6.66 w, 6.47 s, 5.67 s, 5.63 s, 5.55 m, 5.25 s, 5.09 w, 4.90 s, 4.61 w, 4.44 w, 4.43 w, 4.31 m, 3.84 s, 3.83 m, 3.66 s, 3.62 s, 3.59 w, 3.50 m, 3.38 m, 3.33 m.
β - <i>cis</i> -[Co(C ₁₄ H ₁₈ N ₄)Cl ₂] ₂ S ₂ O ₈ ·1½H ₂ O	8.30 m, 7.54 s, 6.87 m, 6.75 s, 6.52 w, 6.04 s, 5.39 s, 5.21 m, 5.11 m, 4.87 m, 4.77 w, 4.25 w, 4.21 w, 4.08 m, 3.72 s, 3.49 w.
β - <i>cis</i> -[Cr(C ₁₄ H ₁₈ N ₄)Cl ₂] ₂ S ₂ O ₈ ·2H ₂ O	8.22 m, 7.57 s, 7.03 s, 6.90 m, 6.49 w, 6.04 s, 5.41 s, 5.32 w, 5.23 m, 4.90 m, 4.80 w, 4.25 w, 4.20 w, 4.14 s, 3.82 m, 3.50 s.

Table 2. Electronic spectral parameters from *cis*-dichloro complexes of chromium(III) and cobalt(III) with 2-aminomethylpyridine and 1,6-bis(2'-pyridyl)-2,5-diaza-hexane.

Compound	λ_{\max} nm (1)	ϵ_{\max} (1)	λ_{\max} nm (2)	ϵ_{\max} (2)
α - <i>cis</i> -[Cr(C ₆ H ₈ N ₂) ₂ Cl ₂]Cl·H ₂ O ^a	540.5	97	402	89.5
α - <i>cis</i> -[Cr(C ₁₄ H ₁₈ N ₄)Cl ₂]Cl·3H ₂ O	545	104	407.5	99
β - <i>cis</i> -[Cr(C ₆ H ₈ N ₂) ₂ Cl ₂]I ^a	534	78	405	95
β - <i>cis</i> -[Cr(C ₁₄ H ₁₈ N ₄)Cl ₂]NO ₃ ·½H ₂ O	538	131	407	100
α - <i>cis</i> -[Co(C ₆ H ₈ N ₂) ₂ Cl ₂]Cl·H ₂ O ^b	538.5	136		
α - <i>cis</i> -[Co(C ₁₄ H ₁₈ N ₄)Cl ₂]Cl·1½H ₂ O	541.5	128	392.5	131
β - <i>cis</i> -[Co(C ₆ H ₈ N ₂) ₂ Cl ₂]Cl·2H ₂ O ^b	534	113		
β - <i>cis</i> -[Co(C ₁₄ H ₁₈ N ₄)Cl ₂]NO ₃ ·½H ₂ O	532	158		

^a Ref. 19. ^b Ref. 17.Table 3. CD-spectral parameters for some complexes of chromium(III) with 1,6-bis(2'-pyridyl)-2,5-diaza-hexane (C₁₄H₁₈N₄), 2-aminomethylpyridine (C₆H₈N₂), 1,10-phenanthroline (C₁₂H₈N₂), 2,2'-bipyridine (C₁₀H₈N₂) and 1,2-ethanediamine (C₂H₆N₂).

Compound	Ligand = L	λ_{ex} (1) nm	$\Delta\epsilon_{\text{ex}}$ (1)	λ_{ex} (2) nm	$\Delta\epsilon_{\text{ex}}$ (2)	λ_{ex} (3) nm	$\Delta\epsilon_{\text{ex}}$ (3)	Ref.
(-) _D -[LCr(OH) ₂ CrL] ⁴⁺	C ₁₄ H ₁₈ N ₄			520	-5.30	382	+1.10	
(+) _D -[LCr(OH) ₂ CrL] ⁴⁺	C ₁₄ H ₁₈ N ₄			520	+5.42	383	-1.13	
(-) _D -[L ₂ Cr(OH) ₂ CrL ₂] ⁴⁺	C ₆ H ₈ N ₂	538	+0.37	508	-5.55	376	+1.62	11
$\Delta\Delta$ (-) _D -[L ₂ Cr(OH) ₂ CrL ₂] ⁴⁺	C ₁₂ H ₈ N ₂			~520	~ -6.2	~400	~ +2.6	5
$\Delta\Delta$ (-) _D -[L ₂ Cr(OH) ₂ CrL ₂] ⁴⁺	C ₁₀ H ₈ N ₂	615	+0.18	518	-6.62	402	+0.79	20
(+) _D -[CrLCl ₂] ⁺	C ₁₄ H ₁₈ N ₄	583	-1.06	511	+1.10	395	-0.12	
(+) _D -[CrL ₂ Cl ₂] ⁺	C ₆ H ₈ N ₂	575	-0.66	513	+0.88	409	-0.17	11
Δ (+) _D -[CrL ₂ Cl ₂] ⁺	C ₂ H ₆ N ₂	590	-0.5	520	+0.6	425	+0.25	22

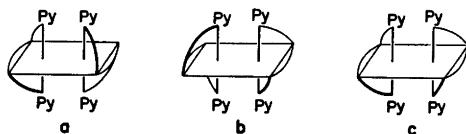


Fig. 3. $[(C_{14}H_{18}N_4)Cr(OH)_2Cr(C_{14}H_{18}N_4)]^{4+}$. a, b and c are the three isomers that can be constructed from two α -*cis*-skeletons. a, Δ (α) Δ (α). b, Δ (α) Δ (β). c, Δ (β) Δ (β).

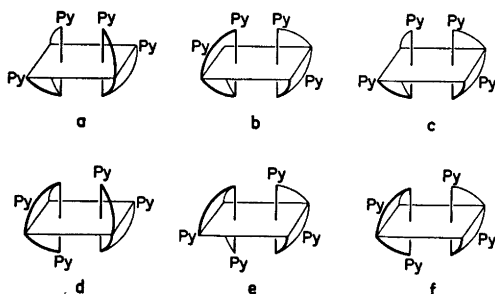


Fig. 4. $[(C_{14}H_{18}N_4)Cr(OH)_2Cr(C_{14}H_{18}N_4)]^{4+}$. a, b, c, d, e and f are the six isomers that can be constructed from two β -*cis*-skeletons. a, Δ (β) Δ (β). b, Δ (β) Δ (β). c, Δ (β) Δ (β). d, Δ (β) Δ (β). e, Δ (β) Δ (β). f, Δ (β) Δ (β).

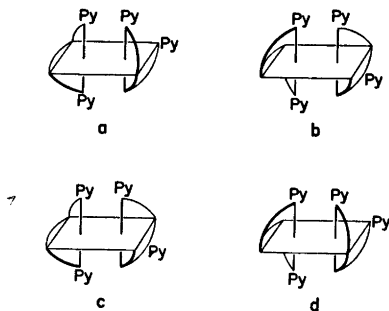


Fig. 5. $[(C_{14}H_{18}N_4)Cr(OH)_2Cr(C_{14}H_{18}N_4)]^{4+}$. a, b, c and d are the four isomers that can be constructed from one α -*cis*-skeleton and one β -*cis*-skeleton. a, Δ (α) Δ (β). b, Δ (α) Δ (β). c, Δ (α) Δ (β). d, Δ (α) Δ (β).

unsymmetrical β -*cis* configuration (Fig. 2c, d). It was possible to isolate racemates of all the predicted compounds and the optically active forms of α -*cis*- $[Cr(C_{14}H_{18}N_4)Cl_2]^+$ (Fig. 2a and b). Gibson and McKenzie¹² assigned the configurations of the cobalt complexes by means of 1H MNR spectra. As we prepared

the α -complex by a totally different method and the β -complex by a slightly different method, we had to repeat the measurements to identify our compounds. Our measurements confirmed the previously found results.

To assign the configurations of the chromium complexes we compared their X-ray powder diffraction patterns with those of the corresponding cobalt complexes. We found strong evidence for isomorphism between blue-violet *cis*- $[Cr(C_{14}H_{18}N_4)Cl_2]ClO_4$ and blue-violet α -*cis*- $[Co(C_{14}H_{18}N_4)Cl_2]ClO_4$ and a reasonable evidence for isomorphism between red-violet *cis*- $[Cr(C_{14}H_{18}N_4)Cl_2]_2S_2O_8 \cdot 2H_2O$ and red-violet β -*cis*- $[Co(C_{14}H_{18}N_4)Cl_2]_2S_2O_8 \cdot 1\frac{1}{2}H_2O$ (Table 1).

Table 2 shows a comparison between the absorption spectra of *cis*- $[M(C_{14}H_{18}N_4)Cl_2]^+$ and *cis*- $[M(C_6H_8N_2)_2Cl_2]^+$ ions, where again $M = Co(III)$ or $Cr(III)$ and $C_6H_8N_2 = 2$ -aminomethylpyridine. We notice the similarity especially regarding the position of the absorption maxima of related compounds.

Stereochemistry of the di- μ -hydroxobis[1,6-(2'-pyridyl)-2,5-diazahehexane]chromium(III) ion. The binuclear ion $[(C_{14}H_{18}N_4)Cr(OH)_2Cr(C_{14}H_{18}N_4)]^{4+}$ in principle exists in several isomeric forms. From an α -*cis*-skeleton for instance (Fig. 2 a and b), we can build up a total of three different isomers (Fig. 3 a, b, c). From a β -*cis*-skeleton we can build six different isomers (Fig. 4 a, b, c, d, e, g), and by the combination of an α -*cis*-skeleton and a β -*cis*-skeleton we can build four different isomers (Fig. 5a, b, c). Molecular models indicate, however, that eleven of these thirteen isomers would be grossly hindered sterically. We are thus left with the probability of finding two isomers only, namely the catoptromers shown in Fig. 3a and b.

Our experiments agreed nicely with that. We found one kind of di- μ -hydroxo complex, a racemate that could be resolved, the $(-)_D$ -isomer accounting for 47 % of the starting material.

On the assumption that the acid cleavage reaction of the di- μ -hydroxobis[1,6-bis-(2'-pyridyl)-2,5-diazahehexane]chromium(III) ion proceeds with retention of configuration as experienced for diols with 2-aminomethylpyridine,¹¹ 1,10-phenanthroline and 2,2'-bipyridine,^{5,20} the catoptromers (Fig. 3a and b) should react with conc. hydrochloric acid to

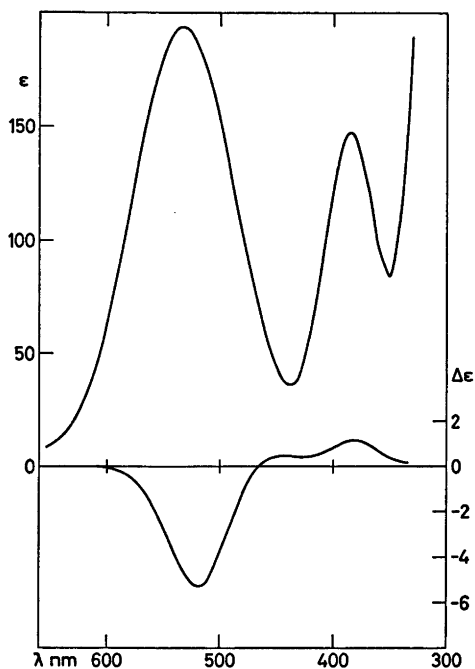


Fig. 6. The absorption spectrum (top) and the circular dichroism spectrum (bottom) of $(-)_D$ - $[(C_{14}H_{18}N_4)Cr(OH)_2Cr(C_{14}H_{18}N_4)]^{4+}$.

form *cis*-dichloro complexes of the symmetrical type shown in Fig. 2a, b. In fact $(+)_D$ - $[(C_{14}H_{18}N_4)Cr(OH)_2Cr(C_{14}H_{18}N_4)](ClO_4)_4 \cdot 4H_2O$ did react solely forming $(+)_D$ - α -*cis*- $[Cr(C_{14}H_{18}N_4)Cl_2]ClO_4$, confirming that our assignments have been correct.

Configuration and optical activity. The absorption and CD spectra of $(-)_D$ - $[(C_{14}H_{18}N_4)Cr(OH)_2Cr(C_{14}H_{18}N_4)]^{4+}$ are shown in Fig. 6, and a comparison with spectral data for corresponding compounds appears in Table 3. If the chirality can be related to the sign of the dominant CD-band in the region of the cubic ${}^4A_{2g} \rightarrow {}^4T_{2g}$ $d-d$ absorption of the chromium(III) ion,²¹ the configurations of $(-)_D$ - and $(+)_D$ - $[(C_{14}H_{18}N_4)Cr(OH)_2Cr(C_{14}H_{18}N_4)]^{4+}$ should be $\Delta\Delta$ and $\Lambda\Lambda$, respectively. Consequently the configuration of $(+)_D$ - α -*cis*- $[Cr(C_{14}H_{18}N_4)Cl_2]^+$ is Λ .

The absorption and CD-spectra of $(+)_D$ - α -*cis*- $[Cr(C_{14}H_{18}N_4)Cl_2]^+$ are shown in Fig. 7, and a comparison with the spectral data for analogous compounds appears in Table 3. The CD-spectrum has the same main features as

Acta Chem. Scand. A 31 (1977) No. 6

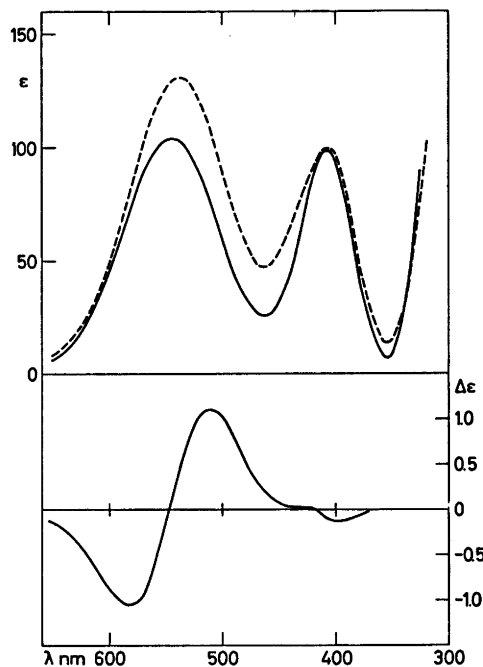


Fig. 7. The absorption spectra (top) of α -*cis*- $[Cr(C_{14}H_{18}N_4)Cl_2]^+$ (—) and β -*cis*- $[Cr(C_{14}H_{18}N_4)Cl_2]^+$ (---) and the circular dichroism spectrum (bottom) of $(+)_D$ - α -*cis*- $[Cr(C_{14}H_{18}N_4)Cl_2]^+$.

the CD-spectra of Λ - $(+)_D$ -*cis*-dichloro complexes of chromium(III) with 2-aminomethylpyridine²¹ and 1,2-ethanediamine²² with a positive, but in this case not dominant, band in the region 510–520 nm.

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