

Octahedral Bis(2-picolyamine) Complexes of Chromium(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 chromium(III) complexes of the general formula $cis\text{-}[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_2\text{X}_2]^{n+}$, where $\text{X} = \text{F}, \text{Cl}, \text{Br},$ and H_2O , have been prepared for the first time, and their absorption spectra have been measured.

X-Ray powder photographs show isomorphism between the so-called $\alpha\text{-}cis\text{-}[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_2\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$ and $\alpha\text{-}cis\text{-}[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$ and between $\beta\text{-}cis\text{-}[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_2\text{Cl}_2]_2\text{S}_2\text{O}_6$ and $\beta\text{-}cis\text{-}[\text{Co}(\text{C}_6\text{H}_8\text{N}_2)_2\text{Cl}_2]_2\text{S}_2\text{O}_6$. This involves that $\alpha\text{-}cis\text{-}[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_2\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$ together with all the compounds belonging to the α -series, probably contain a complex ion with a twofold axis of symmetry, while $\beta\text{-}cis\text{-}[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_2\text{Cl}_2]_2\text{S}_2\text{O}_6$ and the compounds belonging to this series contain a completely unsymmetrical ion. The partial structural assignment of the isomers is based upon the earlier described investigations on the PMR spectra of the corresponding cobalt(III) complexes.

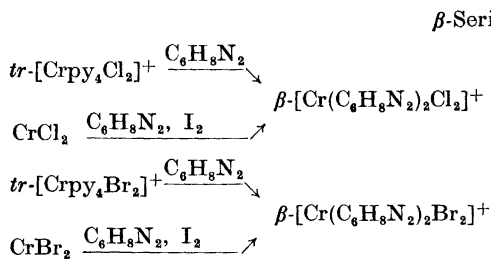
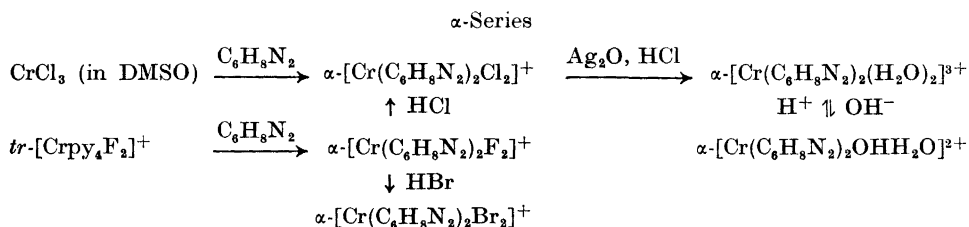
In a recent paper¹ octahedral bis(2-picolyamine) complexes of cobalt(III) were described (2-picolyamine = 2-aminomethylpyridine). Their absorption spectra and PMR spectra made it reasonable to conclude that all the compounds belonging to the so-called β -series had the same configuration, namely a *cis, cis, cis*, and that all complexes belonging to the α -series had the same configuration, namely a *cis, trans, cis* or a *cis, cis, trans*. The isomers were 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.

This paper describes suitable synthetic methods for the preparations of octahedral bis(2-picolyamine) complexes of chromium(III). The ligands in the *cis*-positions are F^- , Cl^- , Br^- , and H_2O . It was again only possible to prepare *cis*-complexes belonging to two series, called α and β .

The chemical reactions and the absorption spectra of the compounds supported the assumption that all the complexes belonging to the α -series had the same amine configuration, and that all the complexes belonging to the β -series had the same amine configuration. X-Ray powder photographs showed isomorphism between α -*cis*-[Cr(C₆H₈N₂)₂Cl₂]Cl·H₂O and α -*cis*-[Co(C₆H₈N₂)₂Cl₂]Cl·H₂O and between β -*cis*-[Cr(C₆H₈N₂)₂Cl₂]₂S₂O₆ and β -*cis*-[Co(C₆H₈N₂)₂Cl₂]₂S₂O₆, establishing thereby the structural relationship between the chromium and the cobalt series.

GENERAL REMARKS CONCERNING THE PREPARATION METHODS

The reaction schemes below represent the pathways by which the different chromium complexes were obtained. The reaction between chromium(III) chloride and a bidentate amine in a suitable medium represents a general method of preparing tris(diamine) or bis(diamine) complexes of chromium.²⁻⁶



trans-Difluorotetrakis(pyridine) chromium(III) salts react with several amines which can replace pyridine.⁷ *trans*-Compounds are most often formed although the use of 2-picolyamine leads to *cis*-compounds. Under certain conditions these reacted with hydrochloric and hydrobromic acid to form α -*cis*-[Cr(C₆H₈N₂)₂Cl₂]Cl and α -*cis*-[Cr(C₆H₈N₂)₂Br₂]Br, respectively, thus establishing a probable structural relationship to these compounds. The property of a fluoro complex, that the fluoride ion through the action of the appropriate strong acid can be replaced by chloride and bromide, is known and used already by several authors.⁸⁻¹⁰

β -*cis*-[Cr(C₆H₈N₂)₂Cl₂]I and β -*cis*-[Cr(C₆H₈N₂)₂Br₂]I were prepared by a method similar to one developed by Glerup and Schäffer.¹¹ Their method

yielded *trans*-dichloro or *trans*-dibromo complexes. In this case the reaction product was a *cis*-complex and even with a β -configuration. This is perhaps due to the fact that β -*cis*-[Cr(C₆H₈N₂)₂Cl₂]I and β -*cis*-[Cr(C₆H₈N₂)₂Br₂]I are insoluble in pyridine, whereas α -*cis*-[Cr(C₆H₈N₂)₂Cl₂]I and α -*cis*-[Cr(C₆H₈N₂)₂Br₂]I are very soluble in pyridine.

The same compounds could be prepared by the reaction in the *heat* between *trans*-dichlorotetrakis(pyridine)chromium(III) iodide and *trans*-dibromotetrakis(pyridine)chromium(III) iodide and 2-picolyamine in 2-methoxyethanol. The reaction is noteworthy, because the same reaction partners in the *cold*, in a slightly different medium and mixed in another ratio, give tris-(2-picolyamine) complexes.¹²

The attempt to prepare a β -aqua complex by the same method as that used for the α -aqua complex, resulted in sticky, impure products.

Several attempts were made in vain to prepare a β -difluoro complex.

EXPERIMENTAL

Reagents. 2-Picolyamine was purchased from Aldrich Co., Inc. and electrolytic chromium from Smelztechnik G.m.b.H., Munich 42, Germany. *trans*-[Crpy₄Cl₂]I and *trans*-[Crpy₄Br₂]I were prepared by methods developed by Glerup and Schäffer.¹¹ *trans*-[Crpy₄F₂]Br·2H₂O and *trans*-[Crpy₄F₂]I were prepared as described before.⁷ All other chemicals were reagent grade and were used without further purification.

PREPARATIONS

1a. α -*cis*-Difluorobis(2-picolyamine)chromium(III) bromide, α -[Cr(C₆H₈N₂)₂F₂]Br. 5.0 g *trans*-[Crpy₄F₂]Br (10.3 mmol) was dissolved in 20 ml 2-methoxyethanol. 4.5 ml 2-picolyamine (43.8 mmol) was added, and the solution was heated with stirring until a red precipitate formed, and pyridine evaporated (approx. 30 min). After cooling on ice, the crystals were filtered and washed with ethanol and acetone; 3.4 g. The crude product was recrystallized twice by dissolving in 10–12 ml boiling water and adding a mixture of 40 ml ethanol and 10 ml ether to the cooled filtrate. Yield: 2.40 g of red-violet, compact crystals (55 % based on chromium). (Found: Cr 12.19; C 34.2; N 13.4; H 4.45; F 9.00; Br 18.9. Calc. for [Cr(C₆H₈N₂)₂F₂]Br·2H₂O: Cr 12.32; C 34.1; N 13.3; H 4.77; F 9.00; Br 18.9.) (ϵ, λ)_{max}: (99.2, 519), (50.2, 373). (ϵ, λ)_{min}: (12.7, 430), (26.2, 347). Half-width: 3325 cm⁻¹. Medium: water.

1b. α -*cis*-Difluorobis(2-picolyamine)chromium(III) iodide, α -[Cr(C₆H₈N₂)₂F₂]I. 12.0 g *trans*-[Crpy₄F₂]I (23 mmol) dissolved in 30 ml 2-methoxyethanol was heated with 12 ml 2-picolyamine (116 mmol) until pyridine evaporated and a red precipitate formed (about 1 h). After cooling on ice, the crystals were filtered and washed with ethanol and acetone; 9.5 g. The product was extracted on the filter with 100 ml boiling water. 30 g sodium iodide was added to the filtrate. Cooling on ice gave a precipitate, which was filtered and washed as above; 8.5 g. The recrystallization was performed by dissolving in 75 ml boiling water and cooling of the filtrate. Pink, needle-shaped crystals separated. Washing as above; 5.2 g. The addition of 20 g sodium iodide to the filtrate gave an extra yield of 1.1 g (total yield: 61 %). (Found: Cr 11.52; C 32.2; N 12.5; H 4.07; F 8.43; I 27.9. Calc. for [Cr(C₆H₈N₂)₂F₂]I·H₂O: Cr 11.53; C 31.9; N 12.4; H 4.03; F 8.42; I 28.1.) (ϵ, λ)_{max}: (98.8, 519), (49.9, 373). (ϵ, λ)_{min}: (12.3, 430), (26.5, 347). Half-width: 3325 cm⁻¹. Medium: water.

2a. α -*cis*-Dichlorobis(2-picolyamine)chromium(III) chloride, α -[Cr(C₆H₈N₂)₂Cl₂]Cl. 3.2 g anhydrous chromium(III) chloride (20 mmol) was suspended in 10 ml dimethyl sulphoxide. 6 ml 2-picolyamine (58 mmol) was added while stirring, and an exothermic reaction took place followed by the precipitation of a bright red compound. 10 ml ethanol was added. After cooling on ice, the red precipitate was filtered and washed with ethanol

and ether. The 7 g pure looking crystals were then extracted on the filter with 90 ml hot water (80°). Cooling on ice resulted in the precipitation of 3.0 g of shining, ruby-red crystals, which were filtered and washed with ethanol and ether. The addition of a solution of 15 g lithium chloride in 30 ml water to the filtrate gave an extra yield of 2.2 g. (Total yield: 67 %.) (Found: Cr 13.23; C 36.8; N 14.6; H 4.61; Cl 27.2. Calc. for $[\text{Cr}(\text{C}_6\text{H}_5\text{N}_2)_2\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$: Cr 13.24; C 36.7; N 14.3; H 4.63; Cl 27.1.) $(\epsilon, \lambda)_{\text{max}}$: (97.0, 540.5), (89.5, 402). $(\epsilon, \lambda)_{\text{min}}$: (20.8, 459), (9.2, 353). Half-width: 3292 cm^{-1} . Medium: 0.1 M hydrochloric acid. When solid sodium iodide was added to the final filtrate, a small amount of brown-red crystals separated. They were identified by the absorption spectrum as β -*cis*- $[\text{Cr}(\text{C}_6\text{H}_5\text{N}_2)_2\text{Cl}_2]\text{I}$.

Salts containing the α -*cis*-dichlorobis(2-picolyamine)chromium(III) ion could be prepared by another method, namely by the reaction in a stoppered flask between the α -*cis*-difluorobis(2-picolyamine)chromium(III) ion and a saturated solution (–16°) of hydrogen chloride.

2b. α -*cis*-Dichlorobis(2-picolyamine)chromium(III) iodide, α - $[\text{Cr}(\text{C}_6\text{H}_5\text{N}_2)_2\text{Cl}_2]\text{I}$. 1.0 g α -*cis*- $[\text{Cr}(\text{C}_6\text{H}_5\text{N}_2)_2\text{F}_2]\text{I}\cdot\text{H}_2\text{O}$ (2.22 mmol) was suspended in a few ml conc. hydrochloric acid in a conical flask (25 ml). The liquid was saturated with gaseous hydrogen chloride at –16°, and the flask was stoppered and left for three days at room temperature. By then red crystals had separated from the first-formed red solution. After cooling the flask was opened, and the crystals were filtered and washed with ethanol and ether. The recrystallization was performed twice by dissolving the product in approx. 30 ml water (80°) and adding a saturated solution of sodium iodide to the cooled filtrate. Washing as above. Yield: 0.51 g (44 %). (Found: Cr 10.30; C 28.8; N 11.1; H 3.92; Cl 14.2; I 25.6. Calc. for $[\text{Cr}(\text{C}_6\text{H}_5\text{N}_2)_2\text{Cl}_2]\text{I}\cdot 2\text{H}_2\text{O}$: Cr 10.36; C 28.7; N 11.2; H 3.61; Cl 14.1; I 25.3.) $(\epsilon, \lambda)_{\text{max}}$: (97.9, 540.4), (92.7, 402). $(\epsilon, \lambda)_{\text{min}}$: (23.6, 458), (16.4, 353). Half-width: 3292 cm^{-1} . Medium: 0.1 M hydrochloric acid to which a small amount of ascorbic acid had been added.

3a. α -*cis*-Dibromobis(2-picolyamine)chromium(III) bromide, α - $[\text{Cr}(\text{C}_6\text{H}_5\text{N}_2)_2\text{Br}_2]\text{Br}$. 2.75 g α -*cis*- $[\text{Cr}(\text{C}_6\text{H}_5\text{N}_2)_2\text{F}_2]\text{Br}\cdot 2\text{H}_2\text{O}$ (6.5 mmol) was suspended in a few ml conc. hydrobromic acid (48 %) in a conical flask (25 ml). The liquid was saturated with gaseous hydrogen bromide at –16°, and the flask was stoppered and left at room temperature for three days. By then red crystals had separated from the first-formed red solution. After cooling on ice, the flask was opened, and the crystals transferred to a glass-filter. Washing with ethanol and ether. The product was extracted with 200 ml water (80°), and the crystals were reprecipitated by the addition of a solution of 20 g lithium bromide in 100 ml ethanol to the filtrate. Cooling, filtering and washing as above; 1.8 g. The crystals were redissolved in 100 ml water (80°). A solution of 10 g lithium bromide in 40 ml ethanol was added to the cooled filtrate, and 1.4 g glistening dark-red crystals separated (41 %). (Found: Cr 9.80; C 27.3; N 10.7; H 3.41; Br 45.9. Calc. for $[\text{Cr}(\text{C}_6\text{H}_5\text{N}_2)_2\text{Br}_2]\text{Br}\cdot\text{H}_2\text{O}$: Cr 9.88; C 27.4; N 10.7; H 3.44; Br 45.6.) $(\epsilon, \lambda)_{\text{max}}$: (95.5, 552), (104, 413.5). $(\epsilon, \lambda)_{\text{min}}$: (28.4, 468), (12.9, 360). Half-width: 3401 cm^{-1} . Medium: 0.1 M hydrochloric acid.

3b. α -*cis*-Dibromobis(2-picolyamine)chromium(III) iodide, α - $[\text{Cr}(\text{C}_6\text{H}_5\text{N}_2)_2\text{Br}_2]\text{I}$. The iodide could be prepared by a method very similar to that of the bromide but with α -*cis*- $[\text{Cr}(\text{C}_6\text{H}_5\text{N}_2)_2\text{F}_2]\text{I}\cdot\text{H}_2\text{O}$ as an initial material. The crude product was recrystallized twice by dissolving in hot water (80°) and adding a saturated solution of sodium iodide to the filtrate. Washing with ethanol and ether. 1.8 g α -*cis*- $[\text{Cr}(\text{C}_6\text{H}_5\text{N}_2)_2\text{F}_2]\text{I}\cdot\text{H}_2\text{O}$ (2.22 mmol) gave a yield of 0.45 g α -*cis*- $[\text{Cr}(\text{C}_6\text{H}_5\text{N}_2)_2\text{Br}_2]\text{I}\cdot\text{H}_2\text{O}$ (35 %). (Found: Cr 9.04; C 25.0; N 9.95; H 3.13; Br 27.8; I 22.7. Calc. for $[\text{Cr}(\text{C}_6\text{H}_5\text{N}_2)_2\text{Br}_2]\text{I}\cdot\text{H}_2\text{O}$: Cr 9.06; C 25.1; N 9.76; H 3.17; Br 27.8; I 22.1.) $(\epsilon, \lambda)_{\text{max}}$: (94.7, 552), (104, 414). $(\epsilon, \lambda)_{\text{min}}$: (28.6, 467), (22.1, 363). Half-width: 3401 cm^{-1} . Medium: 0.1 M hydrochloric acid to which a small amount of ascorbic acid was added.

4a. α -*cis*-Hydroxyaquabis(2-picolyamine)chromium(III) chloride, α - $[\text{Cr}(\text{C}_6\text{H}_5\text{N}_2)_2\text{OH}(\text{H}_2\text{O})\text{Cl}_2]$. 1.40 g α -*cis*- $[\text{Cr}(\text{C}_6\text{H}_5\text{N}_2)_2\text{Cl}_2]\text{Cl}\cdot\text{H}_2\text{O}$ (3.57 mmol) was added to moist silver oxide, freshly prepared from 3.0 g silver nitrate (18 mmol). The filtrate was cooled on ice and acidified with conc. hydrochloric acid. The slow addition of 200 ml ethanol (99 %) and 200 ml ether caused an orange product to precipitate. Filtering and washing with ethanol and ether. Yield: 1.35 g presumed $[\text{Cr}(\text{C}_6\text{H}_5\text{N}_2)_2(\text{H}_2\text{O})_2\text{Cl}_2]\cdot n\text{H}_2\text{O}$. The compound was dissolved in 5 ml water. 5 ml pyridine was added followed by 125 ml ethanol (99 %). The pink crystals that separated were filtered and washed as above. Yield 0.57 g (41 %). (Found: Cr 13.25; C 36.6; N 14.2; H 5.06; Cl 18.3.

Calc. for $[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_2\text{OHH}_2\text{O}]\text{Cl}_2\cdot\text{H}_2\text{O}$: Cr 13.26; C 36.8; N 14.3; H 5.40; Cl 18.1.) $(\epsilon, \lambda)_{\text{max}}$: (83.9, 525), (55.5, 395). $(\epsilon, \lambda)_{\text{min}}$: (33.3, 445), (40.8, 353). Medium: water.

4b. α -cis-Hydroxyaquabis(2-picolylamine)chromium(III) dithionate. α - $[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_2\text{OHH}_2\text{O}]\text{S}_2\text{O}_6$. 0.57 g α -cis- $[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_2\text{OHH}_2\text{O}]\text{Cl}_2\cdot\text{H}_2\text{O}$ (1.45 mmol) was dissolved in 5 ml water. A solution of 0.40 g sodium dithionate, dihydrate (1.65 mmol) in 2 ml water was added. The solution was left for three days. Then the big, glistening, red crystals that had separated were filtered and washed with a small amount of ice-cold water, with ethanol and with acetone. Yield: 0.25 g (37 %). (Found: Cr 11.23; C 30.9; N 12.1; H 4.18. Calc. for $[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_2\text{OHH}_2\text{O}]\text{S}_2\text{O}_6$: Cr 11.22; C 31.1; N 12.1; H 4.13.) $(\epsilon, \lambda)_{\text{max}}$: (83.5, 525), (53.4, 396). $(\epsilon, \lambda)_{\text{min}}$: (33.5, 444), (39.5, 353). Medium: water. The complex could be heated in an oven up to 200° without converting into another compound, as for instance a diol. At 225° complete destruction took place.

5. α -cis-Diaquabis(2-picolylamine)chromium(III) chloride, α - $[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2]\text{Cl}_2$. 0.45 g α -cis- $[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_2\text{OHH}_2\text{O}]\text{Cl}_2\cdot\text{H}_2\text{O}$ (1.15 mmol) was dissolved in 2 ml 4 M hydrochloric acid. A few drops of conc. hydrochloric acid were added. The solution was cooled on ice, and 300 ml ethanol (99 %) and 300 ml ether were added, slowly and while stirring. The orange precipitate was filtered and washed with ethanol (99 %) and ether. Yield: 0.44 g (92 %). (Found: Cr 12.47; C 34.9; N 13.5; H 4.95; Cl 25.8. Calc. for $[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2]\text{Cl}_2\cdot\frac{1}{2}\text{H}_2\text{O}$: Cr 12.48; C 34.6; N 13.5; H 5.00; Cl 25.5.) $(\epsilon, \lambda)_{\text{max}}$: (98.4, 491), (54.3, 367). $(\epsilon, \lambda)_{\text{min}}$: (19.2, 416), (47.2, 351). Half-width: 3580 cm^{-1} . Medium: 0.1 M hydrochloric acid.

6a. β -cis-Dichlorobis(2-picolylamine)chromium(III) iodide, β - $[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_2\text{Cl}_2]\text{I}$. 5.2 g electrolytic chromium (0.10 mmol) was dissolved in 45 ml 6 M hydrochloric acid (0.27 mol). The solution was evaporated in a vacuum rotatory evaporator, and the precipitated chromium(II) chloride was heated in the same equipment until it looked white and dry. 25 g 2-picolylamine (0.23 mol) dissolved in 100 ml pyridine was sucked into the reaction flask, which was then removed from the evaporator and equipped with a condenser. The reaction mixture was refluxed, a solution of 12 g iodine (0.1 mol) in 40 ml pyridine being added slowly. After approx. 30 min the heating was interrupted. The brownish precipitate was filtered and washed with ethanol. Yield: 44 g presumed $[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_2\text{Cl}_2]\text{I}$. Purification: 5 g of the crude product was dissolved in 200 ml hot water (70°). A saturated water solution of 10 g sodium iodide was added to the cooled filtrate to give a purer product, which was filtered and washed with ethanol; 4.2 g. The recrystallization was repeated by dissolving in 160 ml water (70°) and reprecipitating by adding a solution of 10 g sodium iodide to the filtrate. The crystals were washed with ethanol and ether. Yield: 3.6 g of a violet-red powder (68 %). (Found: Cr 11.14; C 30.8; N 12.5; H 3.47; Cl 15.1; I 27.3. Calc. for $[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_2\text{Cl}_2]\text{I}$: Cr 11.16; C 30.9; N 12.0; H 3.47; Cl 15.2; I 27.2.) $(\epsilon, \lambda)_{\text{max}}$: (78.3, 534), (95.0, 405). $(\epsilon, \lambda)_{\text{min}}$: (24.9, 461), (13.2, 353). Half-width: 3713 cm^{-1} . Medium: 0.1 M hydrochloric acid to which a small amount of ascorbic acid had been added.

The same compound could be prepared by another method: 2.50 g $[\text{Crpy}_4\text{Cl}_2]\text{I}$ (4.4 mmol) was dissolved in 15 ml hot 2-methoxyethanol. The solution was heated to near the boiling point of the solvent (124°), and 1.0 ml 2-picolylamine (10 mmol) was added while stirring. The heating was continued for approx. 30 min. Then the reaction mixture was cooled on ice. The red-brown precipitate was filtered and washed with ethanol; 1.51 g. The product was recrystallized once as described above and was then identified by the absorption spectrum as β - $[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_2\text{Cl}_2]\text{I}$. Yield: 1.12 g (55 %).

6b. β -cis-Dichlorobis(2-picolylamine)chromium(III) dithionate, β - $[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_2\text{Cl}_2]_2\text{S}_2\text{O}_6$. 4.7 g β - $[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_2\text{Cl}_2]\text{I}$ (10 mmol) was treated with a suspension of freshly prepared silver chloride (from 4 g silver acetate) in 10 ml water. The solution was filtered from the formed silver iodide and surplus silver chloride. During stirring and cooling, a solution of 4 g lithium chloride dissolved in 200 ml ethanol and 25 ml ether was added. The glistening, red-violet, flaky crystals that separated were filtered, washed with ethanol and ether and identified by their absorption spectrum as β - $[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_2\text{Cl}_2]\text{Cl}$. Yield: 0.60 g (16 %).

0.30 g β -cis- $[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_2\text{Cl}_2]\text{Cl}$ (0.8 mmol) was dissolved in 5 ml hot water (70°). A solution of 1.2 g sodium dithionate, dihydrate, (5.0 mmol) in 3 ml water (70°) was added. Cooling on ice. The red-violet crystals of β - $[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_2\text{Cl}_2]_2\text{S}_2\text{O}_6$ were filtered and washed with ice-water, ethanol and acetone. Yield: 0.29 g (85 % based on the chloride). (Found: Cr 12.32; C 34.1; N 13.2; H 3.89; Cl 16.7. Calc. for $[\text{Cr}(\text{C}_6\text{H}_8\text{N}_2)_2\text{Cl}_2]_2\text{S}_2\text{O}_6$: Cr

12.40; C 34.4; N 13.4; H 3.85; Cl 16.9.) (ϵ, λ)_{max}: (78.4, 534), (95.0, 405). (ϵ, λ)_{min}: (24.6, 461), (12.9, 353). Half-width: 3713 cm⁻¹. Medium: 0.1 M hydrochloric acid.

7. *β*-*cis*-Dibromobis(2-picolyamine)chromium(III) iodide, β -[Cr(C₆H₈N₂)₂Br₂]₂I. 2.6 g electrolytic chromium (0.05 mol) was dissolved in a mixture of 6 ml conc. hydrobromic acid (48 %) and 5 ml water. The solution was evaporated in a vacuum rotatory evaporator, and the precipitated chromium(II) bromide was heated in the same equipment until it was yellow-white and looked dry. Then 12 ml 2-picolyamine (0.11 mmol) dissolved in 70 ml pyridine was sucked into the reaction flask. This was removed and equipped with a condenser. The reaction mixture was refluxed, while 6.3 g iodine (0.05 mol) dissolved in 20 ml pyridine was added slowly. After approx. 30 min the heating was interrupted; the violet precipitate was filtered and washed with ethanol; 24 g. Purification: 3 g of the crude product was extracted on a glass-filter with 2 × 10 ml water (20°). The addition of solid sodium iodide to this filtrate resulted in the precipitation of shining violet crystals, which were filtered and washed with ethanol. They were recrystallized by the same procedure. Yield: 0.8 g. The analyses and the absorption spectrum made it reasonable to assume that the compound was a diol, but the investigations have not yet been finished. (Found: Cr 8.93; C 24.6; N 9.92; H 3.10; I 43.2. Calc. for [(C₆H₈N₂)₂Cr(OH)₂(C₆H₈N₂)₂]₂I₂·5H₂O: Cr 8.91; C 24.7; N 9.54; H 3.80; I 43.5.) The original residue (from the extraction) was thereafter extracted with 160 ml hot water (80°). To the cooled filtrate a saturated solution of 10 g sodium iodide was added to precipitate 1.6 g of steel-grey crystals presumed to be the wanted β -[Cr(C₆H₈N₂)₂Br₂]₂I. They were recrystallized, being dissolved in 160 ml hot water (80°, and slightly acid) and reprecipitated by the addition of a saturated solution of 10 g sodium iodide to the filtrate. Washing with ethanol and ether. Yield: 1.0 g (29 %). The recrystallizations caused a great loss of material. (Found: Cr 9.35; C 26.1; N 10.1; H 2.92; Br 27.8; I 24.0. Calc. for [Cr(C₆H₈N₂)₂Br₂]₂I: Cr 9.37; C 26.0; N 10.1; H 2.91; Br 28.8; I 22.9.) (ϵ, λ)_{max}: (88.5, 544), (111, 414). (ϵ, λ)_{min}: (32.1, 468), (43.2, 367). Half-width: 3920 cm⁻¹. Medium: 0.1 M hydrochloric acid to which a small amount of ascorbic acid had been added. The curve showing the absorption spectrum is extrapolated to the moment when the compound was dissolved.

The same compound could be prepared by another method: 3.30 g [Crpy₄Br₂]₂I (5.0 mmol) was dissolved in 15 ml 2-methoxyethanol. The solution was heated to near the boiling point of the solvent, and 1.0 ml 2-picolyamine (10 mmol) was added with stirring. The heating was continued for about 30 min. A brownish precipitate occurred. After cooling on ice, it was filtered and washed with ethanol. The crude product (approx. 1.8 g) consisted mainly of β -[Cr(C₆H₈N₂)₂Br₂]₂I and of the presumed diol mentioned above. The recrystallization was performed as described in the previous case. Yield: 0.53 g (19 %) of a compound which was identified by the absorption spectrum as pure β -[Cr(C₆H₈N₂)₂Br₂]₂I. It was of great importance to the yield that the water contents in the initial materials and the solvent were small. A relatively high water content favoured the formation of the diol on behalf of the wanted compound. The recrystallization will always cause a great loss of material.

Physical measurements. Electronic absorption spectra were recorded on a Cary Model 14 spectrophotometer. Data for the maxima and minima have been given above as (ϵ, λ), the molar extinction coefficient ϵ in l mol⁻¹ cm⁻¹, the wavelength λ in m μ . The X-ray powder photographs were obtained on a camera of the Guinier type with CuK α radiation. Silicon was used as standard.

RESULTS AND DISCUSSION

Characterization of the isomers. The chloro and bromo complexes of both series crystallize easily and well. They are all soluble in water. α -*cis*-[Cr(C₆H₈N₂)₂Cl₂]₂I and α -*cis*-[Cr(C₆H₈N₂)₂Br₂]₂I are both soluble in solvents like dimethyl sulfoxide, 2-methoxyethanol, and pyridine, differing in that respect from the corresponding β -compounds, which are both insoluble in these solvents. The colour differences between the analogous compounds are noticeable. So far it has not been possible to prepare a fluoro complex belonging

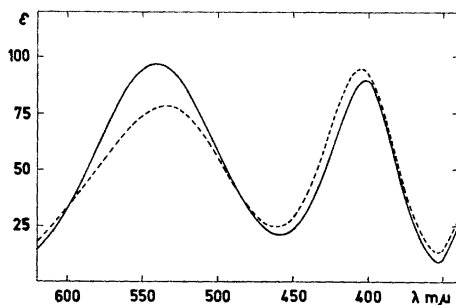


Fig. 1. The absorption spectrum of α -*cis*-[Cr(C₆H₈N₂)₂Cl₂]Cl·H₂O (—) and of β -*cis*-[Cr(C₆H₈N₂)₂Cl₂]I (---). Visible region.

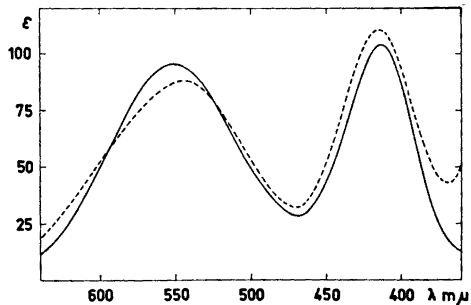


Fig. 2. The absorption spectrum of α -*cis*-[Cr(C₆H₈N₂)₂Br₂]Br·H₂O (—) and of β -*cis*-(Cr(C₆H₈N₂)₂Br₂)I (---). Visible region.

to the β -series, and the aqua complex from the same series could be isolated only as a sticky, impure product, a tendency already noticed for the corresponding cobalt compound.¹

Electronic spectra. The electronic spectra in the visible region of the eight different complex ions are given in Figs. 1–3, and 4. A comparison between the long-wavelength bands (Table 1) shows that the intensities of the α -type bands in all cases are higher than the corresponding β -type bands, which on the other hand occur at higher energies (lower wavelengths). The half-widths of the first band are slightly greater for the β -chloro and bromo complexes (3713 and 3920 cm⁻¹) than for the corresponding α -chloro and bromo complexes

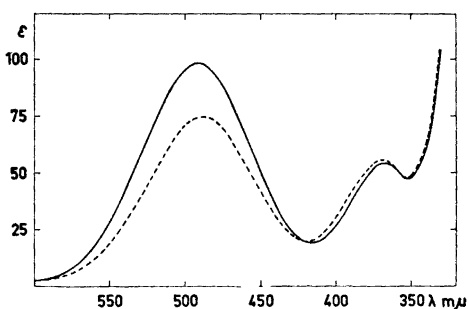


Fig. 3. The absorption spectrum of α -*cis*-[Cr(C₆H₈N₂)₂(H₂O)₂]Cl₂·1/3H₂O (—) and of β -*cis*-[Cr(C₆H₈N₂)₂Cl₂]₂S₂O₈ dissolved in a solution of mercury(II) perchlorate in perchloric acid \sim β -*cis*-[Cr(C₆H₈N₂)₂(H₂O)₂]³⁺ (---). Visible region.

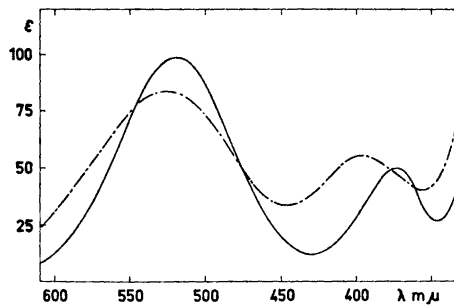


Fig. 4. The absorption spectrum of α -*cis*-[Cr(C₆H₈N₂)₂F₂]I₂·H₂O (—) and of α -*cis*-[Cr(C₆H₈N₂)₂OH·H₂O]Cl₂·H₂O (---). Visible region.

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

Complex	λ_{\max} m μ (1)	ϵ_{\max} (1)	λ_{\max} m μ (2)	ϵ_{\max} (2)
α -[Cr(C ₆ H ₈ N ₂) ₂ F ₂]Br·2H ₂ O	519	99.2	373	50.2
α -[Cr(C ₆ H ₈ N ₂) ₂ Cl ₂]Cl·H ₂ O	540.5	97.0	402	89.5
α -[Cr(C ₆ H ₈ N ₂) ₂ Br ₂]Br·H ₂ O	552	95.5	413.5	104
α -[Cr(C ₆ H ₈ N ₂) ₂ (H ₂ O) ₂]Cl ₃ ·1/3H ₂ O	491	98.4	367	54.3
α -[Cr(C ₆ H ₈ N ₂) ₂ OH(H ₂ O)]Cl ₂ ·H ₂ O	525	83.9	395	55.5
β -[Cr(C ₆ H ₈ N ₂) ₂ Cl ₂]I	534	78.3	405	95.0
β -[Cr(C ₆ H ₈ N ₂) ₂ Br ₂]I	544	88.5	414	111
β -[Cr(C ₆ H ₈ N ₂) ₂ (H ₂ O) ₂] ³⁺ ^a	488	74.9	370	55.5

^a The spectrum of β -[Cr(C₆H₈N₂)₂(H₂O)₂]³⁺ was obtained by measuring a solution of β -[Cr(C₆H₈N₂)₂Cl₂]₂S₂O₆ in a solution of mercury(II) perchlorate (0.2 M) in perchloric acid (0.05 M).

(3292 and 3401 cm⁻¹). This is in agreement with the assumption that the β -complexes are less symmetrical than the α -complexes. Otherwise it is not possible to deduce anything from the differences.

The spectrum of α -*cis*-[Cr(C₆H₈N₂)₂OH(H₂O)]Cl₂·H₂O dissolved in 0.1 M hydrochloric acid is in agreement with the spectrum of α -*cis*-[Cr(C₆H₈N₂)₂(H₂O)₂]Cl₃, confirming that the amine configuration is the same in both cases (Table 2). The spectra of α -*cis*-[Cr(C₆H₈N₂)₂Cl₂]Cl·H₂O and α -*cis*-[Cr(C₆H₈N₂)₂Br₂]Br·H₂O dissolved in a solution of mercury(II) perchlorate (0.2 M) in perchloric acid (0.05 M) have been compared with each other and with the spectrum of α -*cis*-[Cr(C₆H₈N₂)₂(H₂O)₂]Cl₃ (in the acid solution of mercury(II), the complex-bound chloride and bromide are replaced by water). The three spectra agree both with respect to positions and to intensities of the two visible bands (Table 2), confirming the common amine configuration in the compounds.

The amine configuration in α -*cis*-[Cr(C₆H₈N₂)₂F₂]Br cannot be investigated in the same way by a combination of chemical and spectroscopic methods, but,

Table 2. The wavelengths λ_{\max} and the molar extinction coefficients ϵ_{\max} of the absorption bands in the visible region for the α -hydroxyaqua complex measured in 0.1 M hydrochloric acid and for the α - and β -chloro and bromo complexes measured in a solution of mercury(II) perchlorate (0.2 M) in perchloric acid (0.05 M).

Complex	λ_{\max} m μ (1)	ϵ_{\max} (1)	λ_{\max} m μ (2)	ϵ_{\max} (2)
α -[Cr(C ₆ H ₈ N ₂) ₂ OH(H ₂ O)]Cl ₂ ·H ₂ O	491	97.4	367	58.4
α -[Cr(C ₆ H ₈ N ₂) ₂ Cl ₂]Cl·H ₂ O	491	89.1	367	51.1
α -[Cr(C ₆ H ₈ N ₂) ₂ Br ₂]Br·H ₂ O	491	96.8	367	53.1
β -[Cr(C ₆ H ₈ N ₂) ₂ Cl ₂] ₂ S ₂ O ₆	488	74.9	370	55.5
β -[Cr(C ₆ H ₈ N ₂) ₂ Br ₂]I	488	74.9	—	—

Table 3. Data from X-ray powder photographs.

Complex	<i>d</i> -Spacings (Å)				
α - <i>cis</i> -[Co(C ₆ H ₈ N ₂) ₂ Cl ₂]Cl·H ₂ O	7.66 s,	7.15 s,	6.65 s,	5.22 m,	4.93 s,
	4.76 m,	4.71 w,	4.65 w,	4.49 s,	4.10 m,
	4.00 m,	3.84 w,	3.77 w,	3.74 m,	3.70 m,
	3.59 w,	3.49 w,	3.47 w,	3.40 w,	3.38 m,
	3.33 w,	3.30 w,	3.28 w,	3.24 s,	3.22 m.
α - <i>cis</i> -[Cr(C ₆ H ₈ N ₂) ₂ Cl ₂]Cl·H ₂ O	7.73 s,	7.18 s,	6.73 s,	5.27 m,	5.04 s,
	4.81 m,	4.77 w,	4.69 w,	4.55 s,	4.20 m,
	4.04 m,	3.88 w,	3.82 w,	3.77 s,	3.75 m,
	3.65 w,	3.52 w,	3.50 w,	3.45 w,	3.41 w,
	3.38 w,	3.33 w,	3.29 w,	3.26 s,	3.24 m.
β - <i>cis</i> -[Co(C ₆ H ₈ N ₂) ₂ Cl ₂] ₂ S ₂ O ₆	10.5 m,	8.67 s,	7.29 m,	6.55 m,	5.89 s,
	5.84 s,	5.66 w,	5.27 m,	4.97 s,	4.94 m,
	4.38 w,	4.32 m,	4.21 m,	4.14 m,	4.08 w,
	3.95 m,	3.86 w,	3.83 w,	3.72 s,	3.70 s,
	3.67 w,	3.54 m,	3.51 s,	3.32 w,	3.27 s.
β - <i>cis</i> -[Cr(C ₆ H ₈ N ₂) ₂ Cl ₂] ₂ S ₂ O ₆	10.6 m,	8.69 s,	7.25 m,	6.60 m,	5.95 s,
	5.89 s,	5.69 w,	5.28 m,	4.94 s,	4.91 m,
	4.42 w,	4.34 m,	4.24 m,	4.16 m,	4.12 w,
	3.96 m,	3.92 m,	3.85 m,	3.71 s,	3.70 s,
	3.63 w,	3.57 m,	3.52 s,	3.33 w,	3.29 s.

as mentioned before, there is chemical evidence that the amine configuration is the same as for the other α -complexes.

β -*cis*-[Cr(C₆H₈N₂)₂Cl₂]₂S₂O₆ and β -*cis*-[Cr(C₆H₈N₂)₂Br₂]I dissolved in the solution of mercury(II) perchlorate described above give spectra that are in all essentials similar, and that represent the spectrum of the β -*cis*-[Cr(C₅H₈N₂)₂(H₂O)₂]³⁺ ion (Table 2). In the case of the bromo complex, the second band is partly overlapped by an assumed charge-transfer band, which makes a statement of the position and intensity inaccurate. Anyhow, a common amine configuration for the β -complexes is very probable.

X-Ray powder photographs. Table 3 gives the *d*-spacings (calculated from the θ values) for α -*cis*-[Cr(C₆H₈N₂)₂Cl₂]Cl·H₂O, α -*cis*-[Co(C₆H₈N₂)₂Cl₂]Cl·H₂O, β -*cis*-[Cr(C₆H₈N₂)₂Cl₂]₂S₂O₆ and β -*cis*-[Co(C₆H₈N₂)₂Cl₂]₂S₂O₆. The photographs clearly show isomorphism between the α -type complexes of chromium and cobalt and between the β -type complexes of the same two metals.

This involves that all the α -type chromium complexes have the same configuration as the α -type cobalt complexes,¹ namely a *cis*, *trans*, *cis* or a *cis*, *cis*, *trans*, and that the two β -type chromium complexes have the same configuration as the β -type cobalt complexes, namely a *cis*, *cis*, *cis*. Whether, in the first case, the pyridine-nitrogens or the methylamine-nitrogens are in the *trans* positions to each other, is a question that must be left open at the present moment.

REFERENCES

1. Michelsen, K. *Acta Chem. Scand.* **26** (1972) 769.
2. Lindhard, M. and Weigel, M. *Z. anorg. allgem. Chem.* **271** (1952) 115.
3. Schläfer, H. L. and Kling, O. *Z. anorg. allgem. Chem.* **302** (1959) 1.
4. Burstall, F. H. and Nyholm, R. S. *J. Chem. Soc.* **1952** 3570.
5. Pfeiffer, P. and Werdelmann, B. *Z. anorg. allgem. Chem.* **263** (1950) 31.
6. Woldbye, F. *Studier over Optisk Aktivitet*, Polyteknisk forlag, Copenhagen 1969, p. 126.
7. Glerup, J., Josephsen, J., Michelsen, K., Pedersen, E. and Schäffer, C. E. *Acta Chem. Scand.* **24** (1970) 247.
8. Dahme, W., Diss., Clausthal Bergakademie 1957, p. 37.
9. Glerup, J. and Schäffer, C. E. *Chem. Commun.* **1968** 38.
10. Vaughn, J. W., Stvan, O. J. and Magnusson, V. E. *Inorg. Chem.* **7** (1968) 736.
11. Glerup, J. and Schäffer, C. E. *To be published*.
12. Michelsen, K. *Acta Chem. Scand.* **24** (1970) 2003.

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