Acta Chemica Scandinavica A 30 (1976) 521—526

A Double-bridged Binuclear Chromium(III) Complex with 2-Picolylamine. Preparation, Resolution and Stereochemistry of the Di-μ-hydroxo-bis{bis(2-picolylamine)chromium(III)} Ion

KIRSTEN MICHELSEN

Chemistry Department I (Inorganic Chemistry), University of Copenhagen, H. C. Ørsted Institute, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

A new binuclear chromium(III) complex of the double-bridged type $[(C_6H_8N_2)_2Cr(OH)_2Cr(C_6H_8N_2)_2]^{4+}$, where $C_6H_8N_2$ = 2-picolylamine, has been prepared and investigated. The compound, a racemate, has been resolved into its catoptric forms.

Starting from these optically active compounds, *cis*-complexes, $(+)_D$- and $(-)_D$-$[Cr(C_6H_8N_2)_2Cl_2]ClO_4$, have been synthesized. They belong to the earlier described α-series, and their configurations are suggested to be *cis*, *trans*, *cis* because of their origin.

Based on circular dichroism spectra $(-)_D$-$[(C_6H_8N_2)_2Cr(OH)_2Cr(C_6H_8N_2)_2]Cl_4$ and $(-)_D$-α-*cis*-$[Cr(C_6H_8N_2)_2Cl_2]ClO_4$ are assigned the absolute configurations *ΔΔ* and *Δ*, respectively.

In a previous work by the present author [1] concerning octahedral bis(2-picolylamine) complexes of chromium(III) (2-picolylamine = 2-aminomethylpyridine) synthetic methods for the preparation of compounds belonging to two of the possible three series of complexes of the general formula *cis*-$[Cr(C_6H_8N_2)_2X_2]^{n+}$, where X = F, Cl, Br, and H_2O, were described. At that time it was possible to give only a partial assignment of the isomers. In the preparation of one of the compounds, β-*cis*-$[Cr(C_6H_8N_2)_2Br_2]I$, a by-product assumed to be di-μ-hydroxo-bis{bis(2-picolylamine)chromium(III)} iodide, $[(C_6H_8N_2)_2Cr(OH)_2Cr(C_6H_8N_2)_2]I_4.5H_2O$ was isolated. As this di-μ-hydroxo complex reacts with hydrochloric acid to α-*cis*-dichlorobis(2-picolylamine)chromium(III) salts establishing thereby an informative structural relationship between the two types of compounds, a further investigation was considered worth while. In addition, there has been noticeable recent interest in the spectroscopic, kinetic, structural and magnetic properties of binuclear complexes of exactly this type.[2–10]

EXPERIMENTAL

Reagents. 2-Picolylamine was purchased from Aldrich Co. Inc. Chromium(II) chloride was prepared in small portions from electrolytic chromium from Schmelztechnik G.m.b.H., Munich 42, Germany, following the ideas of Lux and Illmann.[11] As a modification the solution containing the chromium(II) ion was evaporated to *dryness* in a vacuum rotatory evaporator, and the precipitated salt was further heated (oilbath, 110 °C) in the same equipment until it looked grayish-green and dry. All other chemicals were of reagent grade and were used without further purifications.

Analyses. The chromium 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.

Physical measurements. Electronic absorption spectra were recorded on a Cary 14 spectrophotometer. The spectra are characterized by their maxima and minima (ε,λ), where the molar extinction coefficient ε is in units of l mol^{-1} cm^{-1} and the wavelength λ is in nm. Optical rotation was measured on a Perkin Elmer 141 polarimeter, and circular dichroism on a Roussel-Jouan Dichrographe I. In all cases the solvent was 0.1 M hydrochloric acid. The magnetic susceptibility of a powdered sample was measured by the Faraday method in the temperature

range 49 – 290 K at a field strength of 15 000 G. The magnetic field was calibrated with $Hg[Co(NCS)_4]$.[12] A more detailed description of the equipment is published elsewhere.[13,14]

Preparations

1a. *Di-μ-hydroxobis{bis(2-picolylamine)chromium(III)}bromide*, $[(C_6H_8N_2)_2Cr(OH)_2Cr(C_6H_8N_2)_2]Br_4.nH_2O$. 4.00 g $[Cr(H_2O)_4Br_2]Br.2H_2O$ (10 mmol) was suspended in 5 ml 2-methoxyethanol, and a spatula of $CrCl_2$ and 2.20 ml 2-picolylamine (21 mmol) was stirred in. After 15 min, ethanol (50 ml 99 %) was added, and the red-violet precipitate was filtered and washed with ethanol and ether; 3.32 g. The crude product was recrystallized by dissolving in water (10 ml) and adding ethanol and ether. Yield 2.82 g (58 %). Anal. $[Cr(C_6H_8N_2)_2OH]_2Br_4.5H_2O$: Cr, C, N, H, Br. In other experiments the complex crystallized with 4 and 4.5 mol of crystal water, respectively. $(\varepsilon,\lambda)_{max}$: (197,540), (117,380). $(\varepsilon,\lambda)_{min}$: (27,436), (59,350). The following two compounds were prepared from 1a by a simple conversion.

1b. *Di-μ-hydroxobis{bis(2-picolylamine)chromium(III)}iodide*, $[(C_6H_8N_2)_2Cr(OH)_2Cr(C_6H_8N_2)_2]I_4.5H_2O$. 1.20 g bromide (*1a*, 1.25 mmol) was dissolved in water (10 ml). 2 g NaI (13 mmol) was added. The solution was heated for a moment and then cooled on ice. Filtering and washing with ethanol; 1.10 g. The crude product was dissolved in boiling water (10 ml), and the filtrate added to a solution of 2 g NaI in water (2 ml). Cooling on ice. Washing with ice-cold water, ethanol, and ether, Yield 1.02 g of shining, flaky, red-violet crystals (70 %). Anal. $[Cr(C_6H_8N_2)_2OH]_2I_4.5H_2O$: Cr, C, N, H, I. $(\varepsilon,\lambda)_{max}$: (198,540), (119,380). $(\varepsilon,\lambda)_{min}$: (29,436), (68,350).

This compound apparently lost all 5 mol of crystal water when heated in an oven for 2 h at 100 °C. The anhydrous complex appeared with a much more bluish colour than the hydrated salt, but the drying had nevertheless left the cation intact, as proved by the absorption spectrum: $(\varepsilon,\lambda)_{max}$: (196,540), (120,380). $(\varepsilon,\lambda)_{min}$: (27,438), 69,350).

1c. *The perchlorate*, $[(C_6H_8N_2)_2Cr(OH)_2Cr(C_6H_8N_2)_2](ClO_4)_4.5H_2O$, was prepared similarly to 1b from the bromide (2.50 g, 2.60 mmol) dissolved in water (10 ml) and $NaClO_4.H_2O$ (4.0 g, 28.5 mmol) dissolved in boiling water (5 ml) 1.05 g (91 %). The crude product was recrystallized from boiling water (15 ml). Washing with ethanol. Yield 1.84 g (67 %). Anal. $[Cr(C_6H_8N_2)OH]_2(ClO_4)_4.5H_2O$: Cr, C, N, H. $(\varepsilon,\lambda)_{max}$: (197,540), (120,380). $(\varepsilon,\lambda)_{min}$: (26,438), (64,350). This compound was used for the magnetic measurements.

2. *Di-μ-hydroxobis{bis(2-picolylamine)chromium(III)}chloride*, $[(C_6H_8N_2)_2Cr(OH)_2Cr(C_6H_8N_2)_2]Cl_4.3\frac{1}{2}H_2O$. The compound was prepared by the same method as the bromide. From 2.66 g $[Cr(H_2O)_4Cl_2].2H_2O$ (10 mmol) and 2.2 ml 2-picolylamine (21 mmol) 1.44 g (37 %) was obtained. Anal. $[Cr(C_6H_8N_2)_2(OH)]_2Cl_4.3\frac{1}{2}H_2O$: Cr, C, N, H, Cl. $(\varepsilon,\lambda)_{max}$: (198,540), (117,380). $(\varepsilon,\lambda)_{min}$: (26,436), (58,350).

3. *Di-μ-hydroxobis{bis(2-picolylamine)chromium(III)} tetrachlorozincate*, $[(C_6H_8N_2)_2Cr(OH)_2Cr(C_6H_8N_2)_2][ZnCl_4]_2.4H_2O$. In this preparation Cr(II) was replaced by zinc powder. 1.33 g $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ (5.0 mmol) was suspended in 3 – 4 ml 2-methoxyethanol, and a spatula of zinc powder and 1.1 ml (11 mmol) 2-picolylamine were stirred in. After 15 min, ethanol (70 ml, 99 %) was added. Filtering and washing with ethanol. The crude product was recrystallized from boiling water. The cooled filtrate directly gave 0.264 g of glistening, red crystals, and the addition of ethanol yielded another crop of 0.166 g. Total yield 16 %. Anal. $[Cr(C_6H_8N_2)_2OH]_2[ZnCl_4]_2.4H_2O$: Cr, C, N, H, Cl. $(\varepsilon,\lambda)_{max}$: (195,540), (114,380). $(\varepsilon,\lambda)_{min}$: (24,438), (57,350).

4a. $(-)_D$-*Di-μ-hydroxobis{bis(2-picolylamine)chromium(III)} antimonyl (+)$_D$-tartrate*, $(-)_D$-$[(C_6H_8N_2)_2Cr(OH)_2Cr(C_6H_8N_2)_2]\{(+)_D$-$SbOC_4H_4O_6\}_4.9H_2O$. 4.00 g $[(C_6H_8N_2)_2Cr(OH)_2Cr(C_6H_8N_2)_2]Br_4.5H_2O$ (4.08 mmol) was dissolved in 30 ml hot water (70 °C). 5.00 g $(+)_D$-$NaSbOC_4H_4O_6$ (16.2 mmol) was dissolved in 20 ml hot water (70 °C). The solutions were mixed, gently heated for a moment and then left in a covered beaker for some hours. By then large, deep red crystals had deposited. They were filtered, thoroughly washed with several portions of ice-cold water and finally with ethanol and ether; 3.45 g (45 %). Anal. $[Cr(C_6H_8N_2)_2OH]_2(SbOC_4H_4O_6)_4.9H_2O$: Cr, C, N, H.

4b. $(+)_D$-*Di-μ-hydroxobis{bis(2-picolylamine)chromium(III)} antimonyl (+)$_D$-tartrate*, $(+)_D$-$[(C_6H_8N_2)_2Cr(OH)_2Cr(C_6H_8N_2)_2]$-$\{(+)_D$-$SbOC_4H_4O_6\}_4.nH_2O$. The mother liquor was set aside for 7 days and then filtered from another crop of 4a (about 75 mg). From the filtrate the desired compound was precipitated by dropwise addition of ethanol (50 ml, 99 %). Filtering and washing with ethanol. The crude product was recrystallized from boiling water (20 ml). Washing with a mixture of ethanol and water (50:50) and with ethanol. Yield 2.17 g of dark, red-violet crystals (29 %). Anal. $[Cr(C_6H_8N_2)_2(OH)]_2(SbOC_4H_4O_6)_4.7H_2O$: Cr, C, N, H.

In other experiments the compound crystallized with 5 or 8 mol of crystal water, respectively.

5a. $(-)_D$-*Di-μ-hydroxobis{bis(2-picolylamine)chromium(III)} chloride*, $(-)_D$-$[(C_6H_8N_2)_2Cr(OH)_2Cr(C_6H_8N_2)_2]Cl_4.4H_2O$. 1.00 g $(-)_D$-$[(C_6H_8N_2)_2Cr(OH)_2Cr(C_6H_8N_2)_2]$-$\{(+)_D$-$SbOC_4H_4O_6\}_4.9H_2O$ (0.533 mmol) was suspended in 7 – 8 ml hot 4 M hydrochloric acid. Stirring for 15 min. By then the originally

coarse crystals had transformed into a fine powder, presumably a tetrachloroantimonate. Filtering and careful washing with conc. hydrochloric acid and ethanol. This powder was then treated with boiling water, whereby a white antimony-compound precipitated, leaving a filtrate from which a sticky red-violet compound would deposit when sufficient ethanol and ether were added. The crude product was recrystallized twice by dissolving in boiling water (3 – 4 ml, slightly acidified with hydrochloric acid), filtering and precipitating with ethanol (50 ml, 99 %) and ether. Washing with ether. Yield 0.363 g (87 %). Anal. $[Cr(C_6H_8N_2)_2OH]_2Cl_4.4H_2O$: Cr, C, N, H, Cl. $(\varepsilon,\lambda)_{max}$: (198,540), (116,380). $(\varepsilon,\lambda)_{min}$: (27,437), (59,350). $[M]_D = -3.19 \times 10^3$ (c = 0.3 g/l).

5b. *(+)$_D$-Di-μ-hydroxobis{bis(2-picolylamine)chromium(III)} chloride,* $(+)_D$-$[(C_6H_8N_2)_2Cr(OH)_2Cr(C_6H_8N_2)_2]Cl_4.nH_2O$. This compound was prepared by exactly the same method as 5a. From 1.40 g $(+)_D$-$[(C_6H_8N_2)_2Cr(OH)_2Cr(C_6H_8N_2)_2]\{(+)_D$-$SbOC_4H_4O_6\}_4.5H_2O$ (0.776 mmol) a yield of 0.470 g (78 %) was obtained. Anal. $[Cr(C_6H_8N_2)_2OH]_2Cl_4.3\frac{1}{2}H_2O$: Cr, C, N, H, Cl, $(\varepsilon,\lambda)_{max}$: (198,540), (116,380). $(\varepsilon,\lambda)_{min}$: (27.437) (59,350). $[M]_D = +3.11 \times 10^3$ (c = 0.3 g/l). In other experiments the compound crystallized with 6 mol of crystal water. The transformation of the compounds 4a and 4b to 5a and 5b could be performed in a more interesting way. An example is given below.

0.70 g of red-violet $(+)_D$-$[(C_6H_8N_2)_2Cr(OH)_2Cr(C_6H_8N_2)_2]\{(+)_D$-$SbOC_4H_4O_6\}_4.5H_2O$ (0.388 mmol) was dissolved in 3 ml 2 m sodium hydroxide. The solution became green, perhaps because of the formation of a di-μ-oxo compound. Ethanol (40 ml, 99 %) was added while stirring to precipitate $NaSbOC_4H_4O_6$. Filtering. Then conc. hydrochloric acid (2 ml) was added to the filtrate recreating the originally red-violet colour of the diol. Sufficient ethanol and ether precipitated a sticky chloride, which was recrystallized as 5a. Yield 0.229 g (72 %). Anal. $[Cr(C_6H_8N_2)_2OH]_2Cl_4.6H_2O$: Cr, C, N, H, Cl. $(\varepsilon,\lambda)_{max}$: (199,540), (118,380). $(\varepsilon,\lambda)_{min}$: (28,437), (60,350). $[M]_D = +3.12 \times 10^3$ (c = 0.3 g/l).

6a. *(−)$_D$-α-cis-Dichlorobis(2-picolylamine)chromium(III) perchlorate,* $(-)_D$-$[Cr(C_6H_8N_2)_2Cl_2]ClO_4.H_2O$. 0.330 g $(-)_D$-$[(C_6H_6N_2)_2Cr(OH)_2Cr(C_6H_8N_2)_2]Cl_4.4H_2O$ (0.421 mmol) was kept in a stoppered flask with conc. hydrochloric acid (3 ml) for 7 days. A very small amount of gray-green powder was then removed by filtration, and perchloric acid (2 ml, 70 %) was added to the filtrate. Cooling on ice gave large red crystals. These were recrystallized from boiling water (10 ml) and washed with ethanol-water (50:50) and with ethanol. Yield 0.132 g (34 %). A careful washing of the compound and a great loss of material in the equipment were responsible for the relatively meagre yield. Anal. $[Cr(C_6H_8N_2)_2Cl_2]ClO_4.H_2O$: Cr, C, N, H, Cl. $(\varepsilon,\lambda)_{max}$: (96,540), (88,402). $(\varepsilon,\lambda)_{min}$: (21,458), (8.7, 353). $[M]_D = -90$ (c = 1 g/l).

6b. *(+)$_D$-α-cis-Dichlorobis(2-picolylamine)chromium(III) perchlorate,* $(+)_D$-$[Cr(C_6H_8N_2)_2Cl_2]ClO_4.H_2O$. The compound was prepared by exactly the same method as 6a. From 0.440 g $(+)_D$-$[(C_6H_8N_2)_2Cr(OH)_2Cr(C_6H_8N_2)_2]Cl_4.3\frac{1}{2}H_2O$ (0.567 mmol) a yield of 0.141 g (27 %) was obtained. Anal. $[Cr(C_6H_8N_2)_2Cl_2]ClO_4.H_2O$: Cr, C, N, H, Cl. $(\varepsilon,\lambda)_{max}$: (96,540), (86,402). $(\varepsilon,\lambda)_{min}$: (21,458), (9.7, 353). $[M]_D = +90$ (c = 1 g/l).

RESULTS AND DISCUSSION

Synthesis and resolution. As the yield of di-μ-hydroxo-bis{bis(2-picolylamine)chromium(III)} iodide in the synthesis intended for *β-cis*-dibromobis(2-picolylamine)chromium(III) iodide was very small,[1] and because the prevalent synthetic method for diols [2,15,16] was unsuccessful in our case, a new preparation method had to be developed. This was partly founded on the preceding experience [1] that chromium(II), present in catalytic amounts, might be responsible for the diol formation, and that an organic solvent was preferable to water. Instead of chromium(II), zinc dust could be used as a catalyst, presumably because of its ability to form chromium(II), but then it was inconvenient because the diol was inevitably precipitated as a tetrachlorozincate.

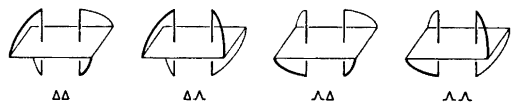

Fig. 1. Configurational isomers for binuclear, double-bridged complexes.

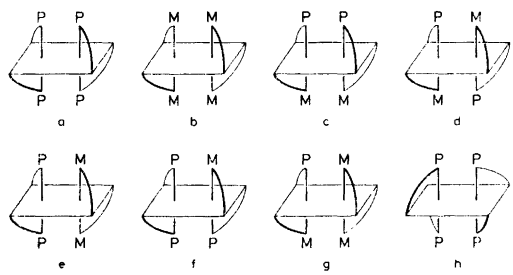

Fig. 2. $[(C_6H_8N_2)_2Cr(OH)_2Cr(C_6H_8N_2)_2]^{4+}$ P symbolizes the pyridine-nitrogen, M the methylaminenitrogen. a – g. ΛΛ isomers. h. A ΔΔ isomer, the optical antipode of a.

Table 1. CD-spectral parameters for some complexes of chromium(III) with 2-picolylamine, 1,10-phenanthroline, 2,2′-bipyridine, ethylenediamine, and trimethylenediamine.

Compound	Ligand = L	$\lambda_{ex}(1)$ nm	$\Delta\varepsilon_{ex}(1)$	$\lambda_{ex}(2)$ nm	$\Delta\varepsilon_{ex}(2)$	$\lambda_{ex}(3)$ nm	$\Delta\varepsilon_{ex}(3)$	$\lambda_{ex}(4)$ nm	$\Delta\varepsilon_{ex}(4)$	Ref.
$(-)_D$-$[L_2Cr(OH)_2CrL_2]^{4+}$	2-picolylamine	588	+0.37	508	−5.55	376	+1.62			
$(+)_D$-$[L_2Cr(OH)_2CrL_2]^{4+}$	2-picolylamine	588	−0.38	508	+5.53	376	−1.65			
$\Delta\Delta$-$(-)_D$-$[L_2Cr(OH)_2CrL_2]^{4+}$	1,10-phenanthroline			~520	~−6.3	~400	+2.6			4
$\Delta\Delta$-$(-)_D$-$[L_2Cr(OH)_2CrL_2]^{4+}$	2,2′-bipyridine	~620	~+0.02	~520	~−6.3	~400	~+1.3			4,22
$(-)_D$-$[CrL_2Cl_2]^+$	2-picolylamine	576	+0.65	513	−0.88	409	+0.17			
$(+)_D$-$[CrL_2Cl_2]^+$	2-picolylamine	575	−0.66	513	+0.88	409	−0.17			
Λ-$(+)_D$-$[CrL_2Cl_2]^+$	ethylenediamine	590	−0.5	520	+0.6	425	+0.25	385	−0.15	20
Λ-$(+)_D$-$[CrL_2Cl_2]^+$	trimethylenediamine	590	−0.36	511	+0.33	419	+0.10	370	+0.10	21

Like the corresponding diols with 1,10-phenanthroline and 2,2′-bipyridine, our compound could be resolved with sodium antimonyl $(+)_D$-tartrate as a resolving agent.[4] In all cases the $(-)_D$-isomer formed the less-soluble diastereoisomer.

The reaction between the catoptromers and conc. hydrochloric acid gave optically active *cis*-dichloro complexes of the so-called α-type. The yields were moderate probably owing to great losses of material during the isolation of the compounds rather than to side-reactions. The complexes were identified as belonging to the α-series[1] by means of their absorption spectra (Fig. 5).

Constitution and stereochemistry of the di-μ-hydroxobis{bis(2-picolylamine)chromium(III)} ion. Alternative formulations of the compound assumed to be $[(C_6H_8N_2)_2Cr(OH)_2Cr(C_6H_8N_2)_2]$-$I_4.5H_2O$ are for instance $[Cr(C_6H_8N_2)_2(H_2O)$-$(OH)]I_2.1H_2O$ and $[(H_2O)(C_6H_8N_2)_2Cr(OH)Cr$-$(C_6H_8N_2)_2(OH)]I_2.4H_2O$. They would be equally consistent with the chemical analyses, and the "anhydrous", watersucking salt (M = 1078) could not be analyzed sufficiently precisely to preclude the possibility of an additional water molecule unambiguously. Nevertheless, we have the following evidence for the double-bridged structure. Firstly: The absorption spectra of the compound dissolved in water and in 0.1 M hydrochloric acid (visible region) are the same. A terminal hydroxo-group would transform fully into an aqua-group under the acid conditions causing a spectral change.[1] Secondly: Measurements of the magnetic susceptibility gave experimental data fitting the Heisenberg-Dirac-Van Vleck model $H = J \times S_2 \times S_2$ for a singlet triplet splitting J of 38 ± 1 cm^{-1} ($\langle g \rangle = 2.00$). As a comparison the value of J is 34 ± 1 cm^{-1} for di-μ-hydroxoxybis{bis-(2,2′-bipyridine)chromium(III)} salts.[17]

The binuclear ion $[(C_6H_8N_2)_2Cr(OH)_2Cr$-$(C_6H_8N_2)_2]^{4+}$ in principle exists in several isomers owing to geometrical and configurational isomerism. The four classes of configurational isomers for dinuclear double-bridged complexes in general are shown in Fig. 1.[18] Molecular models indicate, however, that all the *meso*-isomers in our case would be grossly hindered sterically. Considering now one of the optically active classes, $\Lambda\Lambda$ for instance, we find that seven different isomers

may exist, at least theoretically (Fig. 2a–g). But again we recognize from molecular models that six isomers (Fig. 2b–g) would be grossly hindered, whereas the seventh isomer (Fig. 2a) is relatively free from steric constraints. The seven *ΔΔ* isomers, of course, behave analogously. From this it appears that we are left with a possibility of finding two isomers only (the catoptromers shown in Fig. 2a and h) instead of the theoretical twenty-four (10 *ΔΛ* + 7*ΔΔ* + 7*ΛΛ*). Our experiments agree nicely with this theory. We found exactly one kind of di-μ-hydroxo complex, a racemate that could be resolved, the $(-)_D$-isomer accounting for at least 45 % of the starting material. The two optically active ions are remarkable because they belong to the rarely occurring point group D_2 (one 2-fold axis with two 2-fold axes perpendicular to it).

Stereochemistry of the α-cis-*dichlorobis-(2-picolylamine)chromium(III) ion.* On the assumption that the acid cleavage reaction of the di-μ-hydroxobis{bis(2-picolylamine)chromium(III)} ion proceeds largely with retention of configuration as experienced for diols with 1,10-phenanthroline and 2,2′-bipyridine,[6,4] the catoptromers, Fig. 2a and h, should react with conc. hydrochloric acid to form *cis*-complexes with a 2-fold axis of symmetry as illustrated in Fig. 3.

In fact, our optically active diols did react solely forming *cis*-dichlorobis(2-picolylamine) complexes of the symmetrical α-type, supporting our assumptions about their symmetry properties. *cis*-Complexes of the α-type are earlier shown to have the configuration *cis,trans,cis* or *cis,cis,trans*.[1] 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. On the basis of the reactions above, we now conclude that *cis,trans,cis* is the most likely configuration.

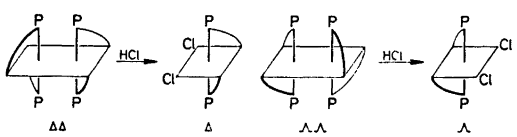

Fig. 3. The reaction of $[(C_6H_8N_2)_2Cr(OH)_2Cr(C_6H_8N_2)_2]^{4+}$ with conc. HCl to *cis*-$[Cr(C_6H_8N_2)_2Cl_2]^{2+}$.

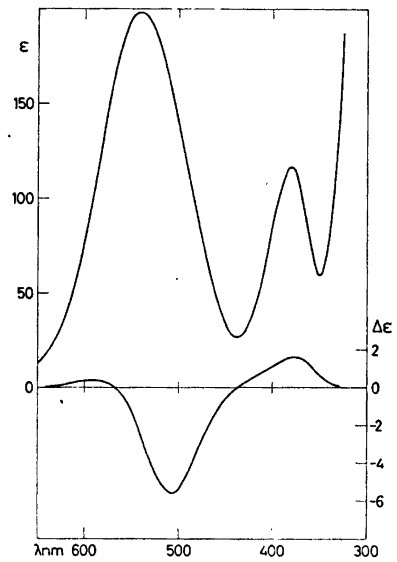

Fig. 4. The absorption spectrum (top) and the circular dichroism spectrum (bottom) of $(-)_D$-$[(C_6H_8N_2)_2Cr(OH)_2Cr(C_6H_8N_2)_2]^{4+}$.

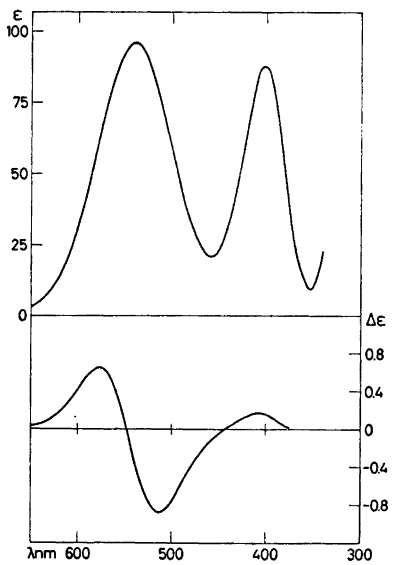

Fig. 5. The absorption spectrum (top) and the circular dichroism spectrum (bottom) of $(-)_D$-α-*cis*-$[Cr(C_6H_8N_2)_2Cl_2]^+$.

Configuration and optical activity. The absorption and circular dichroism (CD) spectra of $(-)_D$-$[(C_6H_8N_2)_2Cr(OH)_2Cr(C_6H_8N_2)_2]^{4+}$ are shown in Fig. 4, and a comparison with CD-spectral data for corresponding compounds appears in Table 1. If the empirical rules [19] relating chirality to the sign of the dominant CD-band in the region of the cubic $^1A_{2g} \rightarrow {}^4T_{2g}d-d$ absorption of the chromium(III) ion can be applied to our compounds, the configurations of $(-)_D$- and $(+)_D$-$[(C_6H_8N_2)_2Cr(OH)_2Cr(C_6H_8N_2)_2]^{4+}$ should be $\Delta\Delta$ and $\Lambda\Lambda$, respectively. Consequently, the configurations of $(-)_D$- and $(+)_D$-α-*cis*-$[Cr(C_6H_8N_2)_2Cl_2]^+$ are Δ and Λ.

The absorption and CD-spectra of $(-)_D$-$[Cr(C_6H_8N_2)_2Cl_2]^+$ are shown in Fig. 5, and the CD-spectral data are listed in Table 1 for this ion, for the catoptromer and for some analogous compounds. The CD-spectrum of $(+)_D$-α-*cis*-$[Cr(C_6H_8N_2)_2Cl_2]^+$ has the same main features as the CD-spectra of Λ-$(+)_D$-$[Cren_2Cl_2]^+$ [20] and Λ-$(+)_D$-$[Crtn_2Cl_2]^+$ [21] with a slightly dominant positive band in the region 510 – 520 nm indicating that this ion, too, has the configuration Λ. This agrees with the assignment suggested above.

Acknowledgement. The author is grateful to Dr. Erik Pedersen for providing the magnetic data.

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Received January 28, 1976.