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Preparations and Partial Structural Assignments of Octahedral *N*,*N'*-Bis(2-pyridylmethyl)-1,2(*R*)-propanediamine Complexes of Cobalt(III) and Chromium(III)

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Complex ions of the general formula *cis*-$[M\{(R)-C_{15}H_{20}N_4\}Cl_2]^+$, where M is cobalt(III) or chromium(III) and $(R)-C_{15}H_{20}N_4$ is the tetradentate amineligand *N*,*N'*-bis(2-pyridylmethyl)-1,2(*R*)-propanediamine (1,6-bis{2-pyridyl}-3(*R*)-methyl-2,5-diazahexane), have been prepared and their stereochemical properties elucidated in some detail.

Two *cis*-α-isomers and eight *cis*-β-isomers are possible for each metal. We isolated all the *cis*-α-isomers, two-β-isomers of cobalt(III) and one *cis*-β-isomer of chromium(III).

The stereochemistry of these complexes is deduced on the basis of ^{13}C NMR spectra, electronic spectra and circular dichroism spectra as well as with the help of chemical reactions which interrelate some of these compounds.

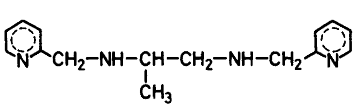

Fig. 1. *N*,*N'*-Bis(2-pyridylmethyl)-1,2(*R*)-propanediamine, bispic(-pn), $C_{15}H_{20}N_4$.

As a natural extension of our earlier work on monomeric and dimeric complexes of trivalent cobalt and chromium with pyridyl-substituted amineligands as 2-pyridylmethylamine,[1–4] 1-(2-pyridyl)ethylamine[5] and *N*,*N'*-bis(2-pyridylmethyl-1,2-ethanediamine (1,6-bis{2-pyridyl}-2,5-diazahexane)[6] we have now investigated the corresponding complexes with the related ligand *N*,*N'*-bis(2-pyridylmethyl)-1,2(*R*)-propanediamine (1,6-bis{2-pyridyl}-3(*R*)-methyl-2,5-diazahexane, abbrev. bispic(-pn), Fig. 1.

As we have emphasized in the previous publications concerning dimeric chromium(III) complexes,[4–6] valuable information can be obtained from the relationship between these types of complexes and the monomeric *cis*-α-complexes.

This paper summarizes the results of our studies on *cis*-dichloro complexes of cobalt(III) and chromium(III) and bispic(-pn) and is a forerunner of a forthcoming work on dimeric chromium(III) complexes with the same ligand.[7] We used preparative methods, that gave mixtures of isomers. In the case of cobalt(III) we succeeded in separating and isolating two *cis*-α-isomers and two *cis*-β-isomers by means of column chromatography. In the case of chromium(III) we obtained two *cis*-α-isomers and one *cis*-β-isomer using fractional crystallization.

Some of the complex species have previously been studied by Bosnich,[8] Brubaker and Cragel.[9] Bosnich presented the absorption and circular dichroism spectra of two compounds he considered to be pure *cis*-α-dichloro complexes of cobalt(III) and chromium(III), respectively, but the methods of preparation were not reported. Brubaker and Cragel prepared a compound regarded to be a pure *cis*-β-dichloro complex of cobalt(III) by air-oxidation of cobalt(II) in the presence of the amine, followed by acidification with hydrochloric acid. The stereochemistry of the compounds was deduced[8,9] from the electronic and circular dichroism spectra. The results of our preliminary studies, however, did not agree with the results obtained by these authors. Therefore, we decided to undertake a new investigation.

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Recently Yamamoto and Shimura[10] have taken an interest in the same type of complexes with bispic(-pn) and have prepared two *cis*-α-isomers of chromium and one *cis*-α-isomer of cobalt. Their results agree with ours.

EXPERIMENTAL

Reagents. Pyridine-2-carboxaldehyde was purchased from Merck-Schuchardt. SP-Sephadex C-25 was purchased from Pharmacia, Uppsala, Sweden. 1,2-Propanediamine was resolved following the method of Dwyer *et al.*[11] *trans*-$[Crpy_4Cl_2]I$ was prepared by a method developed by Glerup and Schäffer.[12] $Na_3[Co(CO_3)_3].3H_2O$ was prepared by the method elaborated by Bauer and Drinkard.[13] All other compounds were of reagent grade and were used without further purification.

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

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 $1 \text{ mol}^{-1} \text{ cm}^{-1}$ and λ is in nm. Circular dichroism was measured on a Roussel-Jouan Dichrographe III in the region 650−200 nm. The extrema are given below as $(\Delta\varepsilon, \lambda) = [(\varepsilon_l - \varepsilon_r), \lambda]$. $[Coen_3]Cl_3.1/2\ NaCl.3H_2O$ was used as a standard, $(\Delta\varepsilon,\lambda) = (1.92,489)$. Optical rotation was measured on a Perkin Elmer Model 141 polarimeter. In all cases the solvent was 0.1 M hydrochloric acid. The ^{13}C NMR spectra were recorded with a Jeol FX 90 Q and a Bruker HX 270 spectrometer both operating in the Fourier transform mode. The chemical shifts δ are relative to $(CH_3)_4Si$. The solvent was d_6-DMSO.

Preparations. 1. *N,N'*-Bis(2-pyridylmethyl)-1,2(*R*)-propanediamine (abbrev. bispic(-pn)), $C_{15}H_{20}N_4$. The ligand was prepared from pyridine-2-carboxaldehyde and $(-)_D$-1,2(*R*)-propanediamine following mainly the methods described by Goodwin and Lions.[14] The crude amine was purified *via* the hydrochloride as described for *N,N'*-bis(2-pyridylmethyl)-1,2-ethanediamine.[6] The pure hydrochloride normally crystallized with 2 mol of crystal water.

2 and 3. $(+)_D$- and $(-)_D$-*cis*-α-Dichloro{*N,N'*-bis(2-pyridylmethyl)-1,2(*R*)-propanediamine}cobalt (III) perchlorate, $(+)_D$- and $(-)_D$-[Cobispic(-pn) $Cl_2]ClO_4$. The compounds were obtained from a crude product containing both the *cis*-α- and *cis*-β-isomers which was prepared using in principle the method of Gibson and McKenzie[15] for *cis*-α-dichloro{*N,N'*-bis(2-pyridylmethyl)-1,2-ethanediamine}cobalt(III) perchlorate.

6.0 g of the compound alleged to be $Na_3[Co(Co_3)_3].3H_2O$ (17 mmol) was suspended in 30 ml water. Bispic(-pn).$2H_2O$ (7.3 g, 17 mmol) was added. When the vigorous effervescence had subsided the solution was boiled for 20 min. Next conc. hydrochloric acid was added, and the boiling was continued until the solution had acquired a blue-violet colour. After 4 days at room temperature a mixture of blue crystals and sodium chloride had separated. The precipitate was left overnight with 25 ml of a solution of mercury(II) perchlorate (0.2 M) in 0.05 M perchloric acid. A solution of diaqua complexes was formed. This solution was diluted 10 times and adsorbed to a short column of SP-Sephadex C 25 ($l \sim 5$ cm, diam. ∼2.5 cm). Mercury(II) was eluted with 0.1 M perchloric acid, and the Sephadex layer with the adsorbed cobalt complexes was transferred to the top of a new column ($l = 50$ cm, diam. = 3.3 cm). Elution with a solution of sodium sulfate (0.1 M) in 0.04 M hydrochloric acid gave two bands, a fast running orange and a slower running red. The eluates with the orange and the red compounds, respectively, were diluted 5 times and adsorbed to short columns where sodium sulfate was eluted with 0.1 M hydrochloric acid. The complexes were eluted afterwards with 2 M hydrochloric acid, and the solutions were evaporated to dryness. The residues were redissolved in 4 M hydrochloric acid and the dichloro complexes precipitated with conc. perchloric acid. Washing with ice-cold water and ethanol.

From the orange band 190 mg was obtained. Anal. $(+)_D$-*cis*-α-$[Co(C_{15}H_{20}N_4)Cl_2]ClO_4$: Co, C, H, N, Cl. $(\varepsilon,\lambda)_{max}$: (121,541.5). $(\varepsilon,\lambda)_{min}$: (19.0,453). $(\Delta\varepsilon,\lambda)_{ex}$: (−1.53,600), (+1.55,520), (+0.41,409).

From the red band 180 mg was obtained. Anal. $(-)_D$-*cis*-α-$[Co(C_{15}H_{20}N_4)Cl_2]ClO_4$: Co, C, H, N, Cl. $(\varepsilon,\lambda)_{max}$: (118,553), $(\varepsilon,\lambda)_{min}$: (19.8,462). $(\Delta\varepsilon,\lambda)_{ex}$: (+1.30,615), (−2.22,533), (−0.91,417).

When the mother liquor was left for a week an extra precipitate was obtained. Separation as above gave 100 mg of the $(+)_D$- and 80 mg of the $(-)_D$-form. Total yields: 3.5 and 3.1 %, respectively.

The addition of perchloric acid to the mother liquor gave a red precipitate (3.65 g), consisting mainly of β-isomers.

Exactly the same compounds (identical absorption and circular dichroism spectra) could be obtained by a similar separation of the crude mixture of isomers we got when we used the established method of air-oxidation of cobalt(II) chloride in the presence of the amine.[9]

4. $(+)_D$-*cis*-β-Dinitro{*N,N'*-bis(2-pyridylmethyl)-1,2(*R*)-propanediamine}cobalt(III) perchlorate,

(+)$_D$-[Cobispic(-pn) $(NO_2)_2$]-ClO_4. The principle of the method, air-oxidation of cobalt(II) in the presence of the amine and sodium nitrite, was adopted from Holtzclaw *et al.*[16] and was earlier used by us in the preparation of a similar compound.[1]

Bispic(-pn).4HCl.2H_2O (4.4 g; 10 mmol) was dissolved in 15 ml 2 M sodium hydroxide (30 mmol). Cobalt(II) 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 5 h. A solution of sodium perchlorate, monohydrate (2 g) was added slowly causing an immediate precipitation of yellow, shining crystals. Filtering and washing with ethanol. Yield: 2.5 – 3.4 g of a mixture of (+)$_D$-*cis*-β-, (−)$_D$-*cis*-β-[Cobispic(-pn)-$(NO_2)_2$]ClO_4 and other isomers in variable ratios. By several recrystallizations from hot 0.005 M perchloric acid a product with a constant absorption and circular dichroism spectrum was obtained.

Anal. (+)D-*cis*-β-[Co($C_{15}H_{20}N_4$)$(NO_2)_2$]ClO_4: Co, C, N, H, Cl. $(\varepsilon,\lambda)_{max}$: (302,446). $(\varepsilon,\lambda)_{min}$: (174,404). $(\Delta\varepsilon,\lambda)_{ex}$: (+2.32,457).

5. (+)$_D$-*cis*-β-Dichloro{*N*,*N*′-bis(2-pyridylmethyl)-1,2(R)-propanediamine}cobalt(III) perchlorate, (+)$_D$-[Cobispic(-pn)Cl_2]-ClO_4. (+)$_D$-*cis*-β-[Copispic(-pn)$(NO_2)_2$]ClO_4 (1.50 g, 2.96 mmol) was suspended in a few ml conc. hydrochloric acid. The mixture was heated on a water-bath (100 °C). A colour-change from yellow *via* orange-red to violet occurred. The solution was evaporated until violet crystals started to separate. Cooling, filtering, and washing with ice-cold water and ethanol (99 %). Yield: ~0.8 g (~56 %). Anal. (+)$_D$-*cis*-β-[Co-($C_{15}H_{20}N_4$)Cl_2]ClO_4: Co, C, N, H, Cl. $(\varepsilon,\lambda)_{max}$: (153,532.5). $(\varepsilon,\lambda)_{min}$: 32.9,454.5). $(\Delta\varepsilon,\lambda)_{ex}$: (+1.03,512), (+0.86,408), (−1.60,323).

The compound was also prepared from the crude mixture of dinitro complexes described in prep. 4. The impure raw product was converted to a mixture of dichloro complexes which on the other hand *via* the diaqua complexes were separated on a column as described in preps. 2 and 3. The compound that was eluted most slowly was the (+)$_D$-*cis*-β-form.

6. (−)$_D$-*cis*-β-Dinitro{*N*,*N*′-bis(2-pyridyl)methyl-1,2(*R*)-propanediamine} cobalt(III) perchlorate, (−)$_D$-[Cobispic(-pn)$(NO_2)_2$]-ClO_4.H_2O. In this preparative method we used the fact that sodium hexanitrocobaltate(III) often reacts with polydentate amines to form dinitro complexes. The method was discovered by Werner and Humphrey.[17] and we have used it earlier in the preparation of a complex with 2-pyridylmethylamine.[1]

Bispic(-pn).4HCl.2H_2O (4.4 g, 10 mmol) was dissolved in 20 ml 2 M sodium hydroxide. The solution was added slowly, while stirring, to a solution of sodium hexanitrocobaltate(III) (4.0 g, 10 mmol) in 20 ml water. The stirring was continued for 1 h. Then a solution of sodium perchlorate, monohydrate (2 g) was added. A yellow precipitate formed immediately. Filtering and washing with ethanol (99 %). Yield: 4.3 g of a mixture of different isomers of [Cobispic(-pn)$(NO_2)_2ClO_4$. The raw product was recrystallized 4 times to obtain a pure compound with a constant absorption and circular dichroism spectrum. Yield: 1.0 g (~19 %). Anal. (−)$_D$-*cis*-β-[Co($C_{15}H_{20}N_4$)$(NO_2)_2$]-ClO_4.H_2O: Co, C, N, H, Cl. $(\varepsilon,\lambda)_{max}$: (331,446.5). $(\varepsilon,\lambda)_{min}$: (201,405). $(\varepsilon,\lambda)_{ex}$: (−1.10,469), (+1.02,417).

7. (−)$_D$-*cis*-β-Dichloro{*N*,*N*′-bis(2-pyridylmethyl)-1,2(*R*)-propanediamine}cobalt(III) perchlorate, (−)$_D$-[Cobispic(-pn)Cl_2]-ClO_4.1/2H_2O. This compound was prepared exactly as described in prep. 5 except that the starting material was (−)$_D$-*cis*-β-(Cobispic(-pn)$(NO_2)_2$]ClO_4.H_2O (0.300 g, 0.57 mmol). The yield was 0.20 g (~71 %). Anal. (−)$_D$-*cis*-β-[Co($C_{15}H_{20}N_4$)Cl_2]ClO_4.1/2 H_2O: Co, C, N, H, Cl and complex-bound Cl. $(\varepsilon,\lambda)_{max}$: (161,532,5). $(\varepsilon,\lambda)_{min}$: (35.9,455). $(\Delta\varepsilon,\lambda)_{ex}$: (+0.43,578), (−0.95,510), (−0.35,420).

The corresponding chromium(III) complexes were prepared by the same two methods that we have used for the preparations of *cis*-α- and *cis*-β-dichloro{*N*,*N*′-bis(2-pyridylmethyl)-1,2-ethanediamine}chromium(III) chloride and dithionate, respectively. One method was based on the reaction between anhydrous chromium(III) chloride and the amine in dimethyl sulfoxide, the other on the reaction between *trans*-dichlorotetrakis(pyridine)chromium(III) iodide in 2-methoxyethanol. Both methods gave mixtures of at least three isomers, but the first reaction was preferable when we wanted the (−)$_D$-*cis*-α-isomer, the second when we wanted the (+)$_D$-*cis*-α-isomer.

8. (−)$_D$-*cis*-α-Dichloro{*N*,*N*′-bis(2-pyridylmethyl)-1,2(*R*)-propanediamine}chromium(III) chloride, (−)$_D$-[Crbispic(-pn)Cl_2].2H_2O.

Method a. Anhydrous chromium(III) chloride (0.80 g, 5.05 mmol) was suspended in dimethyl sulfoxide (8 – 10 ml). Bispic(-pn) (1.3 ml; ~5 mmol) was added slowly. Heating while stirring until the reaction started. Gradually a blue compound precipitated. Cooling and filtering after 1 h. The mother liquor was kept and used for the isolation of a (+)$_D$-*cis*-α- and a (+)$_D$-*cis*-β-isomer (preps. 9a and 10a). The crude product consisting of a practically pure (−)$_D$-*cis*-α-isomer was washed with dimethyl sulfoxide and ethanol (99 %), dissolved in hot 0.1 M hydrochloric acid, filtered and reprecipitated with ethanol and ether. Yield: 0.474 g (21 %). Anal. (−)$_D$-*cis*-α-[Cr($C_{15}H_{20}N_4$)Cl_2]Cl.H_2O: Cr, C, N, H, Cl.

A completely pure compound could be obtained if the chloride was converted to an iodide. 0.200 g (0.44 mmol) was dissolved in hot water (2 ml). Sodium iodide (0.5 g in 1 ml water) was added slowly while stirring. Cooling, filtering and washing with ethanol. Yield: 0.209 g (93 %). Anal. $(-)_D$-*cis*-α-[Crbispic(-pn)Cl_2]I: Cr, C, N, H, Cl, I. $(\varepsilon,\lambda_{max}$: 95.4,554), (90.1,409). $(\varepsilon,\lambda)_{min}$: (22.3,469), (8.4,355). $(\Delta\varepsilon,\lambda)_{ex}$: (+1.24,590), (−1.68,521), (−0.20,427), (+0.44,393).

Method b. trans-[$Crpy_4Cl_2$]I (2.50 g, 4.42 mmol) was suspended in 2-methoxyethanol (10 ml). Bispic (-pn) (1.2 ml, 4.4 mmol) was added slowly. Heating while stirring until the reaction started. A violet product, a mixture of $(+)_D$- and $(-)_D$-*cis*-α-[Crbispic (-pn)Cl_2]I, separated. Cooling, filtering and washing with 2-methoxyethanol and ethanol. The mother liquor was kept and used for the preparation of a $(+)_D$-*cis*-β-isomer (prep. 10b). The $(-)_D$-*cis*-α-isomer was separated from the $(+)_D$-*cis*-α-isomer by an extraction of the crude product with boiling water (3 × 10 ml). Cooling on ice gave blue-violet crystals which were recrystallized from boiling water. Yield: 0.135 g (6.0 %). The absorption and circular dichroism spectra were identical with those of $(-)_D$-*cis*-α-[Crbispic(-pn)Cl_2]I. The residue from the extraction was kept and used for the preparation of a $(+)_D$-*cis*-α-isomer (method 9b).

9. $(+)_D$-*cis*-α-Dichloro{*N*,*N*′-bis(2-pyridylmethyl) -1,2(*R*)-propanediamine} chromium(III) iodide, $(+)_D$-[Crbispic(-pn)Cl_2]I.

Method a. The gradual addition of ethanol and ether to the mother liquor (prep. 8a) gave two precipitates, a lavender-coloured one of moderate size and consisting mainly of $(+)_D$-*cis*-α-[Crbispic(-pn)-Cl_2]Cl and a rose-coloured phase from which we isolated a $(+)_D$-*cis*-β-isomer (prep. 10a). The first precipitate was dissolved in boiling water, sodium iodide was added and finely divided violet crystals of $(+)_D$-*cis*-α-[Crbispic(-pn)Cl_2]I separated out. Yield: 0.402 g (16 %). The compound was recrystallized until the absorption and circular dichroism spectra were constant. Two recrystallizations were normally necessary. Final yield: ~6 %. Anal. $(+)_D$-*cis*-α-[$Cr(C_{15}H_{20}N_4)Cl_2$]I: Cr, C, N, H, Cl, I. $(\varepsilon,\lambda)_{max}$: (103,543), (101,407). $(\varepsilon,\lambda_{min}$: (26.5,463), (13.3,354), $(\Delta\varepsilon,\lambda)_{ex}$: (−1.07,578), (+1.17,510), (−0.07,395).

Method b. The lavender-coloured residue (prep. 8b) was recrystallized from boiling water until the absorption and circular dichroism spectra were constant and in agreement with the spectra reported above. Final yield: ~6 %.

10. $(+)_D$-*cis*-β-Dichloro{*N*,*N*′-bis(2-pyridylmethyl)-1,2(*R*)-propanediamine}chromium(III) iodide, (+)-[Crbispic(-pn)Cl_2]I.1/2H_2O.

Method a. The rose-coloured precipitate (prep. 9a) was dissolved in water, reprecipitated as an iodide by the addition of sodium iodide and recrystallized from boiling water. To obtain reasonable yields it was convenient to recrystallize combined raw products from various batches. Final yield: ~2 % per batch. Anal. $(+)_D$-*cis*-β-[Cr ($C_{15}H_{20}N_4$)Cl_2]I: Cr, C, N, H, Cl, I. $(\varepsilon,\lambda)_{max}$: (129,538), (104,406). $(\varepsilon,\lambda)_{min}$: (45.5,463), (20.1,353). $(\Delta\varepsilon,\lambda)_{ex}$: (−0.21,583), (+1.58,514), (−0.19,395).

Method b. When the mother liquor (prep. 8b) was left for some hours a red-violet precipitate, consisting mainly of $(+)_D$-*cis*-β-[Crbispic(-pn)Cl_2]I separated out. Recrystallizations as above gave a final yield of 2 %. The spectra were in agreement with the data reported above.

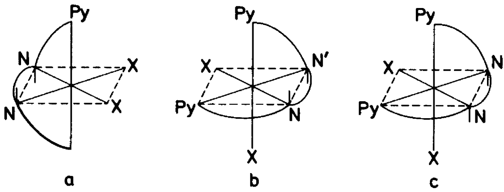

Fig. 2. cis-α- and *cis*-β-[$MbispicenX_2$]$^+$. M = Co(III) or Cr(III). Bispicen = *N*,*N*′-bis(2-pyridyl-methyl)-1,2-ethanediamine, $C_{14}H_{18}N_4$. Py symbolizes the pyridine nitrogen. a, Λ-*cis*-α-{*SS*}; b, Λ-*cis*-β-{*RR*′}; c, Λ-*cis*-β-{*SR*′}.

RESULTS AND DISCUSSION

Stereochemistry of the compounds. The general formula *cis*[$M(C_{14}H_{18}N_4)X_2$]$^+$, where M is cobalt (III) or chromium(III) and $C_{14}H_{18}N_4$ is the tetradentate ligand *N*,*N*′-bis(2-pyridylmethyl)-1,2-ethanediamine (bispicen), includes two types of geometrical isomers, namely isomers with the symmetrical *cis*-α-configuration (Λ-*cis*-α and Δ-*cis*-α) represented in Fig. 2a by the enantiomer with the configuration Λ around the central atom, and isomers with the unsymmetrical *cis*-β-configuration (Λ-*cis*-β and Δ-*cis*-β) represented in Figs. 2b and c by the enantiomers with the configuration Λ around the central atom.

Sargeson and Searle[18] drew attention to the fact that one of the secondary nitrogen atoms in the *cis*-β-[$CotrienX_2$] ion (trien is the tetradentate ligand triethylenetetramine) can coordinate in two different ways while the other secondary nitrogen atom is bound to a fixed position. In the case of the *cis*-α-[$CotrienX_2$]$^+$ ion both secondary nitrogen atoms are forced to take up fixed positions.

Similarly the asymmetry of the coordinated secondary nitrogen atoms in the *cis*-β-[M ($C_{14}H_{18}N_4$)Cl_2]$^+$ ion creates two enantiomeric

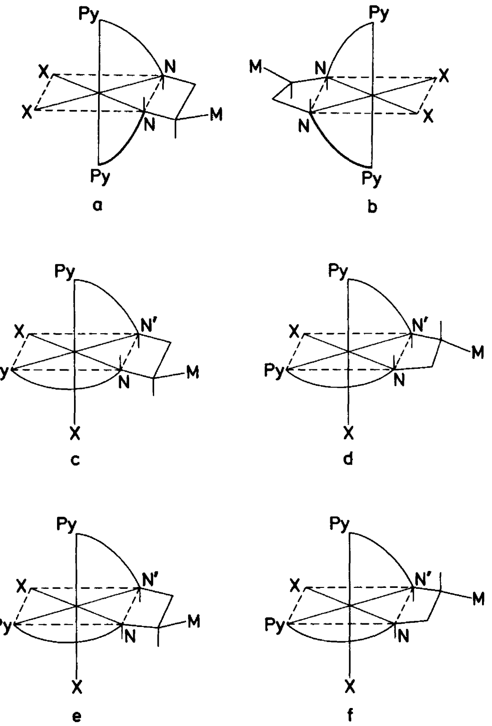

Fig. 3. *cis*-α- and *cis*-β-[Mbispic(-pn)]$^+$. M = Co(III) or Cr(III). Bispic(-pn) = *N*,*N*′-bis(2-pyridyl- methyl)-1,2(*R*)-propanediamine. a, Δ-*cis*-α-{*SR*}; b, Λ-*cis*-α-{*RS*}; c, Λ-*cis*-β-{*SR*′}; d, Λ-*cis*-β-{*RS*′}; e, Λ- *cis*-β-{*RR*′}; f, Λ-*cis*-β-{*SS*′}.

pairs: Λ-*cis*-β-{*RR*′}, Fig. 2b (and the enantiomer Δ-*cis*-β-{*SS*′}) and Λ-*cis*-β-{*SR*′}, Fig. 2c (and the enantiomer Δ-*cis*-β-{*RS*′}.*

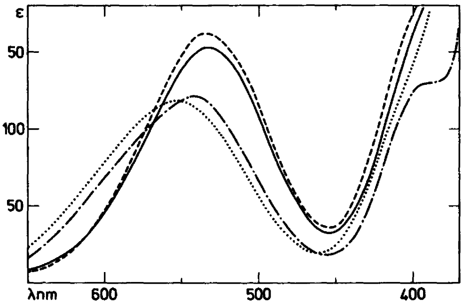

Fig. 4. The absorption spectra (vis. region) of four isomers of [Cobispic(-pn)Cl$_2$]$^+$. Δ-$(-)_{\rm D}$-*cis*-α-{*SR*} (...); Λ-$(+)_{\rm D}$-*cis*-α-{*RS*} (-.-); Δ-$(-)_{\rm D}$-*cis*-β (– – –); Λ-$(+)_{\rm D}$-*cis*{*SR*′} or {*RS*′} (——).

Only one enantiomeric pair is probable for the *cis*-α-[M($C_{14}H_{18}N_4$)X$_2$]$^+$ ion, namely Λ-*cis*-α-{*SS*}, Fig. 2a and Δ-*cis*-α-{*RR*}.

When the ligand is replaced by the closely related ligand *N*,*N*′-bis(2-pyridylmethyl)-1,2(*R*)-propanediamine, $C_{15}H_{20}N_4$, bispic(-pn), and assuming the methyl group in the five-membered chelate ring to occupy an equatorial position,[20] we get ten different isomers. The two *cis*-α-isomers, Δ-*cis*-α-{*SR*} and Λ-*cis*-α-{*RS*}, are shown in Figs. 3a and b. The eight *cis*-β-isomers are: Λ-*cis*-β-{*SR*′}, Λ-*cis*-β-{*RS*′}, Λ-*cis*-β-{*RR*′} and Λ-*cis*-β-{*SS*′}, Δ-*cis*-β-{*RS*′}, Δ-*cis*-β-{*SR*′}, Δ-*cis*-β-{*SS*′} and Δ-*cis*-β-{*RR*′}. The Λ-isomers are shown in Figs. 3c – f.*

^{13}*C NMR.* In a *cis*-β-dichloro complex of cobalt

Table 1. The ^{13}C NMR chemical shifts are reported in ppm downfield from $(CH_3)_4Si$ in DMSO-d$_6$ for the pyridine carbon atoms of *cis*-dichloro complexes of cobalt(III) with *N*,*N*′-bis(2-pyridylmethyl)-1,2(*R*)-propanediamine, (*R*)-$C_{15}H_{20}N_4$ = L.

Compound	Chemical shifts δ ppm for the pyridine carbon atoms									
$(+)_{\rm D}$-α-[CoLCl$_2$]$^+$	165.7		152.8		139.9		124.3		121.8	
$(-)_{\rm D}$-α-[CoLCl$_2$]$^+$	163.9		154.6	154.3	140.1		124.0		123.0	
$(+)_{\rm D}$-β-[CoLCl$_2$]$^+$	165.4	163.5	152.0	150.4	140.2	139.6	125.5	125.3	123.2	122.6
$(-)_{\rm D}$-β-[CoLCl$_2$]$^+$	165.9	164.0	153.7	148.9	140.6	139.7	125.7		123.5	122.2

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* In order to distinguish between the secondary atoms, the atom which is in *cis*-positions to both the atoms X is denoted N′. *R* and *S* refer to the absolute configuration of the coordinated nitrogen atoms following the rules of Cahn *et al.*[19]

* It is important to notice that the *RS* representation of the configuration of the secondary nitrogen groups may result in some confusion. The Λ-*cis*-α-{*SS*}-isomer of [CobispicenX$_2$]$^+$, for instance, corresponds to the Λ-*cis*-α-{*RS*}-isomer of [Cobispic(-pn)X$_2$]$^+$, the Λ-*cis*-β-{*RR*′}-isomer of [CobispicenX$_2$]$^+$ corresponds to the Λ-*cis*-β-{*SR*′}- and the Λ-*cis*-β-{*RS*′}-isomers of [Cobispic-(pn)X$_2$]$^+$.

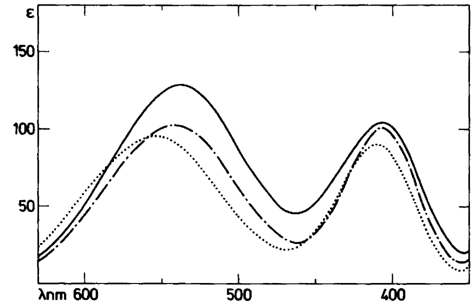

Fig. 5. The absorption spectra (vis. region) of three isomers of $[\mathrm{Crbispic(\text{-}pn)Cl_2}]^+$. Δ-$(-)_\mathrm{D}$-*cis*-α-$\{SR\}$ (...); Λ-$(+)_\mathrm{D}$-*cis*-α-$\{RS\}$ (-.-); Λ-$(+)_\mathrm{D}$-*cis*-β (——).

(III) with bispic(-pn) we would expect ten resonances corresponding to the ten different pyridine-carbon atoms in the molecule. In a corresponding *cis*-α-complex we would expect that the pseudo two-fold axis would reduce the number of resonances to half, or that the ten resonances would lie very closely in pairs. We find (Table 1) that the number of resonances for two of the compounds are reduced to five or six, and that the resonances for the remaining two are ten or nine. We conclude, therefore, that the first two compounds (preps. 2 and 3) in all probability are α-isomers while the other compounds (preps. 5 and 7) are β-isomers. These assignments are in agreement with the spectroscopical and chemical results.

Electronic spectra. The electronic spectra (visible region) of four *cis*-dichloro complexes of cobalt (III) and three *cis*-dichloro complexes of chromium (III) with bispic(-pn) are presented in Figs. 4 and 5.

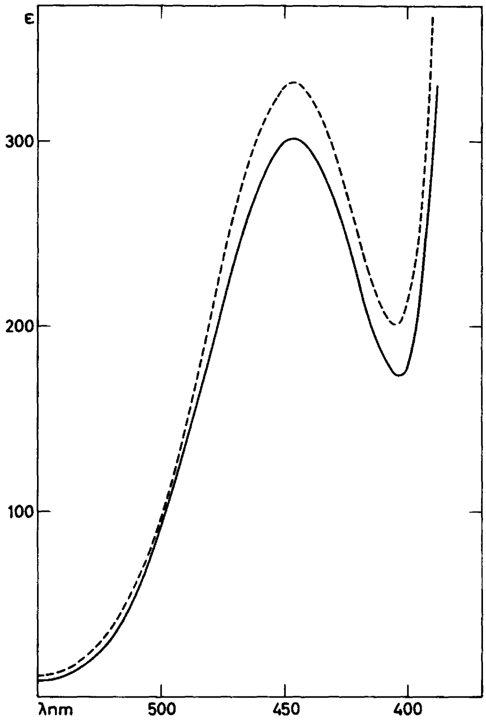

Fig. 6. The absorption spectra (vis. region) of two isomers of $[\mathrm{Cobispic(\text{-}pn)\ (NO_2)_2}]^+$. Δ-$(-)_\mathrm{D}$-*cis*-β (– – –); Λ-$(+)_\mathrm{D}$-*cis*-β-$\{SR'\}$ or $\{RS'\}$ (——).

The great likeness between cobalt and chromium complexes is noticed. A comparison between the long-wavelength bands (Table 2) with those of the corresponding *cis*-α- and *cis*-β-complexes with bispicen[6] reveals a great mutual similarity that

Table 2. Electronic spectral parameters from *cis*-dichloro complexes of cobalt(III) and chromium(III) with *N*,*N*′-bis(2-pyridylmethyl)-1,2-ethanediamine, $C_{14}H_{18}N_4$, and *N*,*N*′-bis(2-pyridylmethyl)-1,2(*R*)-propaneamine, (*R*)-$C_{15}H_{20}N_4$.

Compound	Ligand	λ_{max}nm(1)	ε_{max}(1)	λ_{max}nm(2)	ε_{max}(2)	Ref.
cis-α-$[\mathrm{CoLCl_2}]^+$	$C_{14}H_{18}N_4$	541.5	128			6
$(+)_\mathrm{D}$-*cis*-α-$[\mathrm{CoLCl_2}]^+$	(*R*)-$C_{15}H_{20}N_4$	541.5	121			prep. 2
$(-)_\mathrm{D}$-*cis*-α-$[\mathrm{CoLCl_2}]^+$	(*R*)-$C_{15}H_{20}N_4$	553	118			prep. 3
cis-β-$[\mathrm{CoLCl_2}]^+$	$C_{14}H_{18}N_4$	532	158			6
$(+)_\mathrm{D}$-*cis*-β-$[\mathrm{CoLCl_2}]^+$	(*R*)-$C_{15}H_{20}N_4$	532.5	153			prep. 5
$(-)_\mathrm{D}$-*cis*-β-$[\mathrm{CoLCl_2}]^+$	(*R*)-$C_{14}H_{20}O_4$	532.5	161			prep. 7
cis-α-$[\mathrm{CrLCl_2}]^+$	$C_{14}H_{18}N_4$	545	104	407.5	99	6
$(+)_\mathrm{D}$-*cis*-α-$[\mathrm{CrLCl_2}]^+$	(*R*)-$C_{15}H_{20}N_4$	543	103	407	101	prep. 9
$(-)_\mathrm{D}$-*cis*-α-$[\mathrm{CrLCl_2}]^+$	(*R*)-$C_{15}H_{20}N_4$	554	95.4	409	90	prep. 8
cis-β-$[\mathrm{CrLCl_2}]^+$	$C_{14}H_{18}N_4$	538	131	407	100	6
$(+)_\mathrm{D}$-*cis*-β-$[\mathrm{CrLCl_2}]^+$	(*R*)-$C_{15}H_{20}N_4$	538	129	406	104	prep. 10

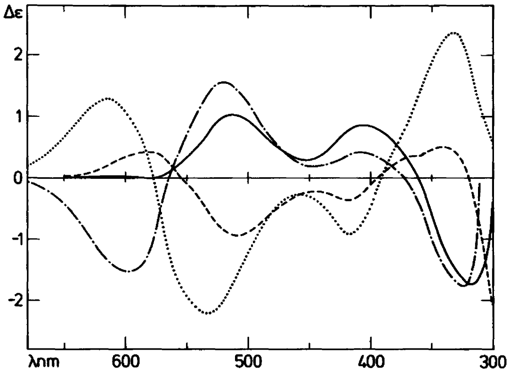

Fig. 7. The circular dichroism spectra (680 – 300 nm) of four isomers of $[Cobispic(-pn)Cl_2]^+$. Δ-(−)$_D$-*cis*-α-{*SR*} (...); Λ-(+)$_D$-*cis*-α-{*RS*} (-.-); Δ-(−)$_D$-*cis*-β (— — —); Λ-(+)$_D$-*cis*-β-{*SR′*} or {*RS′*} (——).

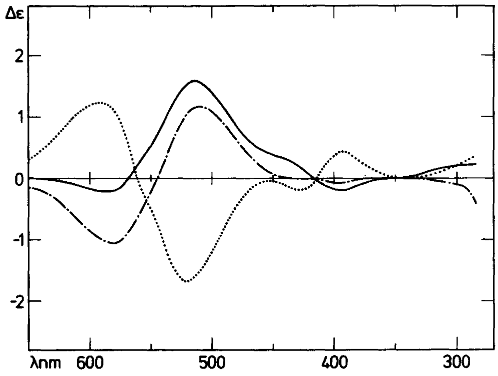

Fig. 8. The circular dichroism spectra (650 – 300 nm) of three isomers of $[Crbispic(-pn)Cl_2]^+$. Δ-(−)$_D$-*cis*-α-{*SR*} (...); Λ-(+)$_D$-*cis*-α-{*RS*} (-.-); Λ-(+)$_D$-*cis*-β (——).

makes the proposed assignment probable. The intensities of all the β-type bands are higher than those of α-type which on the other hand occur at higher wavelengths (lower energies). Fig. 6 shows the uncharacteristic absorption spectra of two dinitro complexes which constituted the starting materials for the preparation of the *cis*-β-dichloro complexes of cobalt.

Circular dichroism spectra. The CD-spectra of the dichloro complexes (vis. region), Fig. 7 and Fig. 8, confirm the assignments given above. The mutual likeness, especially between the α-type complexes of cobalt and chromium is noticed again. The CD-spectral data are listed in Table 3 for these and for some analogous compounds. The preliminary results from an X-ray analysis of $(+)_D$-$[\{(S)(-)_D$-$C_7H_{10}N_2\}_2Cr(OH)_2Cr\{(S)(-)_D$-$C_7H_{10}N_2\}_2]$-$(S_2O_6)_2.2H_2O$,[5,21] where $C_7H_{10}N_2$ is 1-(2-pyridyl)ethylamine, prove that this compound has the configuration ΛΛ. This is in agreement with the empirical rule that relates a dominant positive CD-band in the region of the cubic $^4A_{2g} \rightarrow {}^4T_{2g}$ *d*−*d* absorption of the chromium(III) ion to a ΛΛconfiguration.[22,23] This and other binuclear complexes[4–7] have a dominant CD-band between 505 and 520 nm. They react with conc. hydrochloric acid to form *cis*-α-dichloro complexes having CD-spectra, which show two extrema in the first absorption region, one between 575 and 585 nm and another between 510 and 520 nm. Neither of these bands is particularly dominant but the sign of the latter is the same as the sign of the dominant band for the parental compound. As this sign is positive in the case of all the (+)$_D$-*cis*-α-complexes they are

Table 3. CD-spectral parameters from *cis*-dichloro complexes of cobalt(III) and chromium(III) with *N*,*N′*-bis(2-pyridylmethyl)-1,2-ethanediamine, $C_{14}H_{18}N_4$, and *N*,*N′*-bis(2-pyridylmethyl)-1,2(*R*)-propanediamine, (*R*)-$C_{15}H_{20}N_4$.

Compound	Ligand	λ_{ex}nm(1)	$\Delta\varepsilon_{ex}(1)$	λ_{ex}nm(2)	$\Delta\varepsilon_{ex}(2)$	λ_{ex}nm(3)	$\Delta\varepsilon_{ex}(3)$	Ref.
Λ-(+)$_D$-α-$[CrL_2Cl_2]^+$	$C_6H_8N_2$	575	−0.66	513	+0.88	409	−0.17	4
Λ-(+)$_D$-α-$[CrLCl_2]^+$	$C_{14}H_{18}N_4$	583	−1.06	511	+1.10	395	−0.12	6
(+)$_D$-α-$[CrLCl_2]^+$	(*R*)-$C_{15}H_{20}N_4$	578	−1.07	510	+1.17	395	−0.07	prep. 9
(−)$_D$-α-$[CrLCl_2]^+$	(*R*)-$C_{15}H_{20}N_4$	590	+1.24	521	−1.68	393	+0.44	prep. 8
(+)$_D$-β-$[CrLCl_2]^+$	(*R*)-$C_{15}H_{20}N_4$	583	−0.21	514	+1.58	395	−0.19	prep. 10
(+)$_D$-α-$[CoLCl_2]^+$	(*R*)-$C_{15}H_{20}N_4$	600	−1.53	520	+1.55	409	+0.41	prep. 2
(−)$_D$-α-$[CoLCl_2]^+$	(*R*)-$C_{15}H_{20}N_4$	615	+1.30	533	−2.22	417	−0.91	prep. 3
(+)$_D$-β-$[CoLCl_2]^+$	(*R*)-$C_{15}H_{20}N_4$			512	+1.03	408	+0.86	prep. 5
(−)$_D$-β-$[CoLCl_2]^+$	(*R*)-$C_{15}H_{20}N_4$	578	+0.43	510	−0.95	420	−0.35	prep. 7

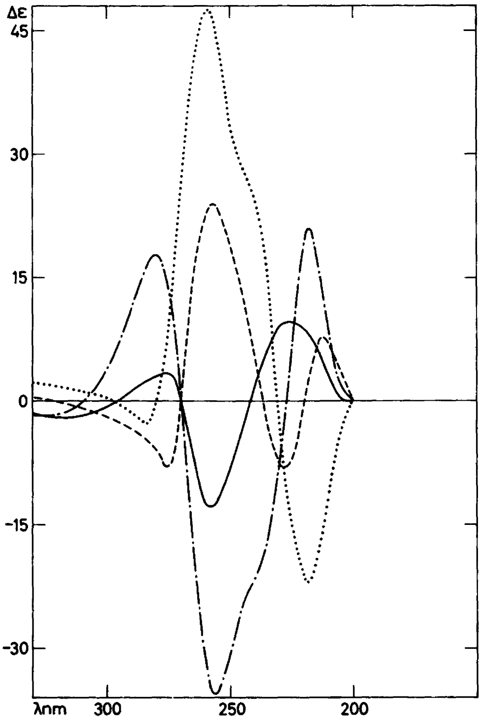

Fig. 9. The circular dichroism spectra (330 – 200 nm) of four isomers of [Cobispic(-pn)Cl$_2$]$^+$. Δ-(−)$_D$-*cis*-α-{*SR*} (...); Λ-(+)$_D$-*cis*-α-{*RS*} (-.-); Δ-(−)$_D$-*cis*-β (– – –); Λ-(+)$_D$-*cis*-β-{*SR*′} or {*RS*′} (——).

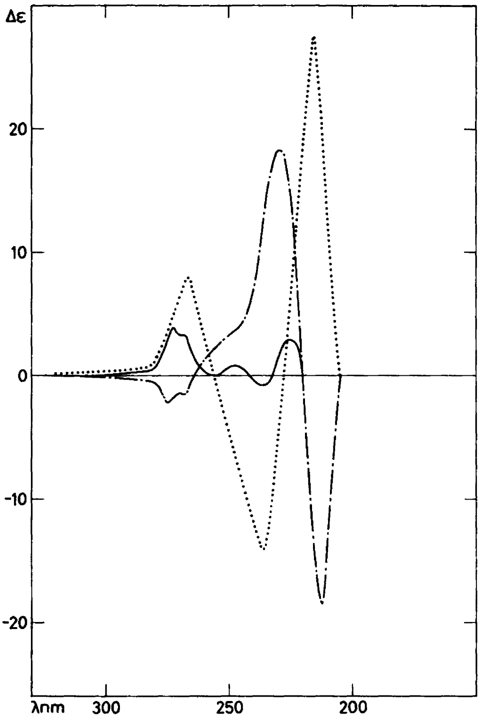

Fig. *10.* The circular dichroism spectra (330 – 200 nm) of three isomers of [Crbispic(-pn)Cl$_2$]$^+$. Δ-(−)$_D$-*cis*-α-{*SR*} (...); Λ-(+)$_D$-*cis*-α-{*RS*} (-.-); Λ-(+)$_D$-*cis*-β (——).

assigned the configuration Λ while the (−)$_D$-*cis*-α-isomers are assigned the configuration Δ. The assignment is transferred to the cobalt complexes. The configuration of the secondary nitrogen atoms are bound to be {*RS*} for all the *cis*-α-isomers (Figs. 3a and b).

The *cis*-β-complexes are characterized by a dominant band in the region 510 – 515 nm. The sign of this band is used to assign the configuration Λ to the (+)$_D$-*cis*-β-isomers, the configuration Δ to the single (−)$_D$-*cis*-β-isomer.

The CD-spectra of the same compounds in the region 330 – 200 nm are shown in Fig. 9 and Fig. 10. The shapes of the curves for all the *cis*-α-complexes are very much alike, but it is noteworthy that the signs of corresponding bands of cobalt and chromium compounds are reversed. The *cis*-β-complexes are all characterized by bands of relatively low intensities.

The CD-spectrum (Fig. 11) of (−)$_D$-[Cobispic(-pn)(NO$_2$)$_2$]ClO$_4$ (prep. 6) is not a typical *cis*-β-spectrum.[24,25] The compound, however, reacts with conc. hydrochloric acid to form Δ-(−)$_D$-*cis*-β-[Cobispic(-pn)Cl$_2$]ClO$_4$ (prep. 7), and this dichloro complex when dissolved in a solution of sodium nitrite and left for 24 h is reconverted to the original starting material. At present we find it probable that the compounds have the same configurations. The CD-spectrum in the UV-region (Fig. 12) looks very similar to that of another *cis*-β-dinitro complex (see below).

We are not able to conclude anything about the configuration of the secondary nitrogen atoms in the molecule.

The CD-spectrum (Fig. 11) of (+)$_D$-[Cobispic(-pn)(NO$_2$)$_2$]ClO$_4$ (prep. 4) has a strong resemblance to the spectrum of Λ-(+)$_D$-*cis*-β-[Cotrien(NO$_2$)$_2$]ClO$_4$,[24] and the compound is assigned the same configuration. This is in agreement with its chemical behaviour. As we have described (prep. 5),

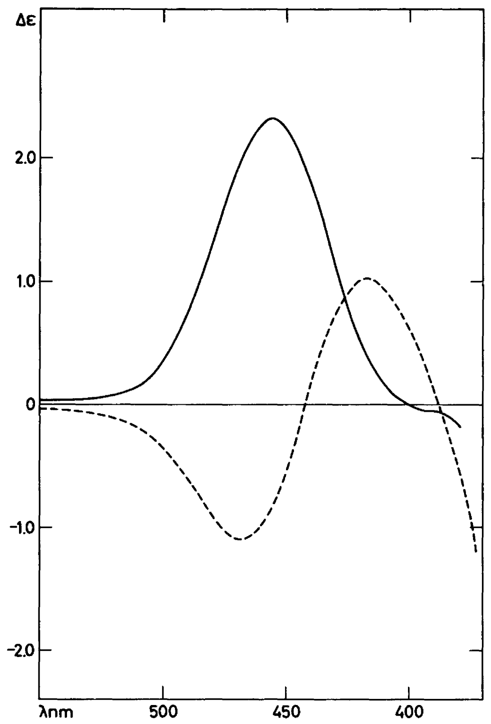

Fig. 11. The circular dichroism spectra (550–370 nm) of two isomers of [Cobispic(-pn) $(NO_2)_2]^+$. Δ-$(-)_D$-*cis*-β (— — —); Λ-$(+)_D$-*cis*-β-{*SR*′} or {*RS*′} (——).

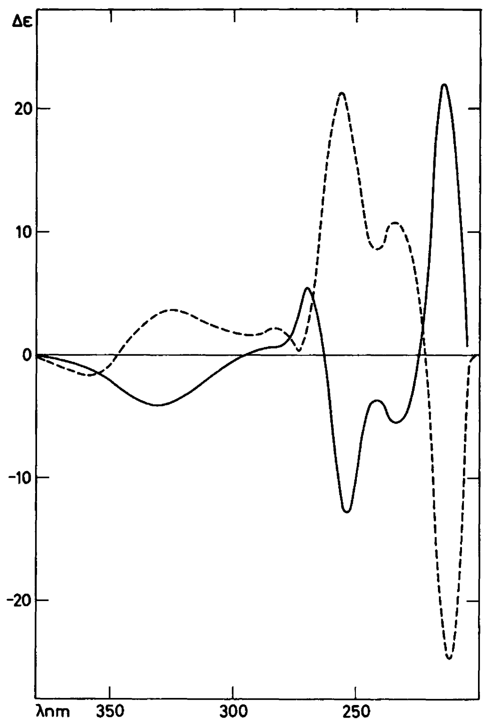

Fig. 12. The circular dichroism spectra (380–200 nm) of two isomers of [Cobispic(-pn) $(NO_2)_2{}^+$. Δ-$(-)_D$-*cis*-β (— — —); Λ-$(+)_D$-*cis*-β-{*SR*′} or {*RS*′} (——).

the complex reacts with conc. hydrochloric acid to form Λ-$(+)_D$-*cis*-β-[Cobispic(-pn)-Cl_2]ClO_4. This dichloro complex, when dissolved in a solution of sodium nitrite and left for 24 h, re-created the dinitro complex. Δ-$(-)_D$-*cis*-α-[Cobispic(-pn)Cl_2]ClO_4 (Fig. 3a, prep. 3), when dissolved in a solution of sodium nitrite and left for 24 h, gave the same compound. A conversion of a Δ-*cis*-α-isomer (Fig. 3a) into a Λ-*cis*-β-isomer most naturally leads to an isomer with the configuration {*SR*′} or {*RS*′} Figs. 3b and c). The secondary nitrogen atoms in Λ-$(+)_D$-*cis*-β-[Cobispic(-pn)Cl_2]-ClO_4 consequently have the same nitrogen configuration.

So far we are not able to say anything conclusive about the configuration of the secondary nitrogen atoms in Λ-$(+)_D$-*cis*-β-[Crbispic(-pn)Cl_2]I.

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