The Preparation and Optical Activity of the Isomers of the 1,2-Cyclopentanediamine Cobalt(III) and Chromium(III) Complexes

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The tris-complexes of (±)-trans-1,2-cyclopentanediamine (± cptn) with Co(III) and Cr(III) were prepared and, contrary to an earlier proposal, they were shown to be monomeric. The Co(III) complexes of − cptn were separated into lel_3 and ob_3 isomers. The single crystal CD-spectrum of $\varLambda$-lel_3-$[Co(-cptn)_3]Cl_3.4H_2O$ diluted in the hexagonal $\varLambda$-lel_3-$[Rh(-chxn)_3]Cl_3.4H_2O$ (− chxn = (−)-trans-1,2-cyclohexanedi-amine) was recorded with light propagating along the crystallographic c-axis which is parallel to the molecular threefold axis, and the result was used for the assignment of the components of the CD-spectra. cis-1,2-Cyclopentanediamine was prepared and the tris-complexes with Co(III) resolved, and further separated into the two geometrical isomers with C_1 and C_3 symmetry, respectively.

In their classical works on complexes with dissymmetrical ligands, Jaeger and Blumendal [1–3] discussed complexes of trans-1,2-cyclopentanediamine (± cptn) with Co(III), Cr(III), Rh(III), and Pt(II). They considered these as monomeric chelate tris- and bis-complexes. Phillips and Royer [4] believed, however, that ± cptn were unable to form chelate complexes because of the long distance between the two nitrogen atoms in the free diamine. After several physico-chemical measurements they concluded that the actual composition of Jaeger's cobalt tris-complex was $[Co_2(\pm cptn)_7(H_2O)_2]^{6+}$. We started our work to clarify this problem from the visible absorption spectrum alone. We found, however, the circular dichroism spectrum of the resolved complex to be so different from that expected that we decided to study further the properties of the possible isomers.

Recently Saito et al. [5] published the results of the X-ray structure analysis of $\varLambda$-lel_3-$[Co(+cptn)_3]Cl_3.4H_2O$.

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From some of the experiments made in an attempt to improve the method of preparation of *trans*-1,2-cyclopentanediamine we obtained the corresponding *cis*-diamine. Tris-complexes of this amine were expected to be more similar to those of other known tris-diamine complexes.

EXPERIMENTAL

Materials

trans-Dichlorotetrakis(pyridine)cobalt(III) chloride, *trans*-[Copy$_4$Cl$_2$]Cl.aq. was prepared by Glerup *et al.*:[6] Cobalt(II) chloride was dissolved in a mixture of methanol and pyridine and was oxidized with chlorine.

cis-Dichlorotetrakis(dimethyl sulfoxide)chromium(III) chloride, *cis*-[Cr(DMSO)$_4$Cl$_2$]-Cl.DMSO, was prepared from a solution of green hydrated chromium(III) chloride, [Cr(H$_2$O)$_4$Cl$_2$]Cl.2H$_2$O in dimethyl sulfoxide from which water was removed by distillation according to E. Pedersen.[7]

trans-Difluorotetrakis(pyridine)chromium(III) perchlorate, *trans*-[Crpy$_4$F$_2$]ClO$_4$, was prepared according to Glerup *et al.*[8]

SE-Sephadex C-25 was obtained from Pharmacia, Uppsala, Sweden. All other chemicals were of "reagent grade" and were used without further purification.

Physical measurements. Absorption spectra in the range $300-700$ nm were measured 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 λ in nm.

Circular dichroism was measured on a Roussel-Jouan Dichrographe I. The extrema of the spectra are given by $(\varepsilon_1 - \varepsilon_r, \lambda) = (\Delta\varepsilon, \lambda)$.

Thermogravimetry was performed on the thermobalance described previously.[9]

NMR spectra were recorded on a Varian A-60 instrument with time average computer (C.A.T. 1024 A).

Measurements of the magnetic susceptibilities were made by the Faraday method. The instrument has been briefly described previously.[10]

Preparations

anti-1,2-Cyclopentanedione dioxime. A modification of Cope's method [11] was used. 38 g of granulated sodium and 900 ml of benzene, dried over sodium, was placed in a 3 l round bottomed flask, equipped with a mechanical stirrer and a condenser. 225 ml of adipic acid diethylester (1.11 mol) was quickly added, followed by 5 ml of 99.9 % ethanol. The mixture was refluxed with stirring during 18 h, then cooled to 0°C, and the precipitate was filtered on a Büchner funnel. The white product was washed with a little benzene and dried in vacuum over paraffin. The yield was approximately 180 g (1.0 mol) of sodium 2-carbethoxycyclopentanonate. The product was partly dissolved in 600 ml of ice-water and nitrogen passed through the solution for 15 min to remove oxygen. A solution of 4 g of sodium hydroxide (0.1 mol) and 70 g of sodium nitrite (1.03 mol) in 160 ml of water was added dropwise. The reaction mixture was heated to 40°C for 30 h with vigorous stirring in the absence of air, then recooled to 0°C. 200 ml of 6 M sulfuric acid (1.2 mol) was then added during 1 h. When the evolution of carbon dioxide had stopped the solution was neutralized with 12 M ammonia. A solution of 70 g of hydroxylammonium chloride (1.01 mol) in 150 ml of water, neutralized with approximately 70 g of potassium carbonate (0.5 mol), was immediately added. After 1 h the precipitation of the light tan needle shaped crystals of the crude *anti*-1,2-cyclopentanedione dioxime was almost completed, and this product was filtered, washed with a little water, and dried for 48 h with concentrated sulfuric acid in an evacuated desiccator. Yield of crude product: 90 g, corresponding to 62 % calculated from adipic acid diethylester.

amphi-1,2-Cyclopentanedione dioxime was isolated as the yellow-brown bis(*amphi*-1,2-cyclopentanedione dioximato)nickel(II) by slowly adding a solution of 20 g of

nickel(II) sulfate heptahydrate in 50 ml of water to the mother liquor from the precipitation of the *anti*-dioxime. The nickel complex was washed with water and air dried. Yield approximately 30 g.

Bis(anti-1,2-cyclopentanedione dioximato)nickel(II). 12.8 g of *anti*-1,2-cyclopentanedione dioxime (0.1 mol) was dissolved in 15 ml of 4 M ammonia and a solution of 12.0 g of nickel(II) chloride hexahydrate (0.05 mol) in 40 ml of water was slowly added with stirring. The red precipitate was filtered, washed with water and dried in air. Yield 11 g, corresponding to 70 % from the dioxime. (Found: C 38.2; H 4.4; N 17.6. Calc. for $NiC_{10}H_{14}N_4O_4$: C 38.4; H 4.5; N 17.9.)

(±)-trans-*1,2-Cyclopentanediamine.* A modification of Jaeger's method [1] was used. A solution of 20 g of *anti*-1,2-cyclopentanedione dioxime (0.156 mol) in 1.5 l of 99.5 % ethanol was placed in a 3 l three-necked round bottomed flask, equipped with a mechanical stirrer, a condenser and a thermometer. After heating to 40°C, 8 g of magnesium powder and 0.1 g of mercury(II) chloride were added. 150 g of sodium (6.5 mol) was then added through the condenser in portions of 5 g with stirring. The temperature was kept below 50°C. The reaction mixture was finally heated to boiling in order to remove unreacted sodium. The diamine was isolated by steam distillation. The distillation flask was heated externally to maintain small volume in the flask. The distillate was collected until pH was below 8 (approximately 4 l). This was acidified (pH = 3) with 12 M hydrochloric acid and evaporated to almost dryness at room temperature in vacuum. The excess of hydrochloric acid was removed by washing with 20 ml of a 2:1 v/v mixture of ethanol and ether, and the hygroscopic 1,2-cyclopentanediamine dihydrochloride was dried with potassium hydroxide in an evacuated desiccator. Yield approximately 5 g, corresponding to 18 % based on the dioxime. In 50 ml of a 1:1 v/v mixture of methanol and ether, 1.7 g of sodium (0.074 mol) was dissolved with cooling. 5 g of the dihydrochloride (0.029 mol) was added in small portions with stirring. After 1 h the precipitated sodium chloride was filtered off and extracted with 5 ml of a 1:1 v/v mixture of methanol and ether. The combined filtrates were evaporated in vacuum to 3 ml and this residue was distilled in nitrogen atmosphere at 13.5 torr. The fraction with b.p.$_{13.5}$ 65−67°C was collected. Yield of *trans*-1,2-cyclopentanediamine 2.5 g, corresponding to 89 % based on the hydrochloride. The product was stored under nitrogen at −20°C.

(−)-trans-*1,2-Cyclopentanediamine.* 2 g of (±)-*trans*-1,2-cyclopentanediamine (0.02 mol) was added to a solution of 7 g of (+)-tartaric acid (0.047 mol) and 1 ml of methanol in 7 ml of water. At 40°C, 12 ml of methanol was added dropwise. The solution was kept for 18 h at 3°C and the crystalline hydrogentartrate was filtered, washed with 10 ml of methanol and dried in air. Yield of crude product 5.2 g, corresponding to 65 % of the racemic diamine. In a 2 % aqueous solution $[\alpha]_D^{25} = +11.3°$. M.p. 128−130°C. The product was recrystallized twice from 30 % v/v methanol in water with a temperature drop from 60°C to 3°C. Yield of long white needles of (−)-*trans*-1,2-cyclopentanediammonium (+)-hydrogentartrate: 2.5 g, corresponding to 31.4 % of the racemic diamine. In a 2 % aqueous solution $[\alpha]_D^{25} = +10.1°$. M.p. 134−135°C. (Found: C 38.9; H 6.3; N 6.9. Calc. for $C_{13}H_{24}N_2O_{12}$: C 39.0; H 6.0; N 7.0.) 2.4 g of this product (0.006 mol) was dissolved in 8 ml of water and potassium hydrogentartrate precipitated by the dropwise addition of a solution of 0.9 g of potassium chloride (0.012 mol) in 4 ml of water. After 1 h the precipitate was filtered off and by the addition of 8 g of potassium hydroxide to the filtrate the solid diamine hydrate separated and was extracted five times with 10 ml portions of ether. The combined extracts were dried with potassium hydroxide and evaporated to dryness. Yield of (−)-*trans*-1,2-cyclopentanediamine 0.55 g, corresponding to 92 % based on the hydrogentartrate.

cis-*1,2-Cyclopentanediamine.* 30 g of potassium tetrahydridoborate was dissolved at 0°C in 600 ml of "diglyme" ("diglyme" = 2,4,7-trioxanonane) in a 2 l flask. 79 g of bis-(*amphi*-1,2-cyclopentanedione dioximato)nickel(II) (0.5 mol) dried with sulfuric acid in vacuum, was added. Nitrogen was passed through the mixture. During 1 h a solution of 25 g of anhydrous aluminium chloride in 100 ml of diglyme was carefully added dropwise under vigorous evolution of hydrogen. The temperature was kept below 35°C by cooling in ice-water. When the evolution of hydrogen had stopped, the mixture was heated to 70°C for 18 h. A solution of 100 g of potassium hydroxide in 150 ml of water was carefully added and the *cis*-diamine isolated by steam distillation. 6 l of distillate was collected, acidified to pH = 3 with 12 M hydrochloric acid, and evaporated under vacuum to almost dryness. The dihydrochloride was washed with a 1:4 v/v ether-ethanol

mixture and dried in vacuum with potassium hydroxide. Yield of *cis*-1,2-cyclopentane-diammonium chloride: 23 g, corresponding to 27 % based on nickel complex. *cis*-1,2-Cyclopentanediamine was isolated as described for the ($\pm$)-*trans*-diamine. B.p.$_{13.5}$ 62 − 65°C. Yield 11 g, corresponding to 83 % based on the dichloride. As expected no resolution was possible with (+)-tartrate.

Tris-{(−)-trans-*1,2-cyclopentanediamine*}*cobalt(III)*   *chloride,*   *tetrahydrate,*   [Co-(−cptn)$_3$]Cl$_3$.4H$_2$O. To a solution of 1.5 g of [Copy$_4$Cl$_2$]Cl.6H$_2$O (2.5 mmol) in 3 ml of 2-methoxyethanol was dropwise added a mixture of 0.75 g of (−)-*trans*-1,2-cyclopentane-diamine (7.5 mmol) and 1 ml of 2-methoxyethanol. The red tris-complex precipitated at once and was filtered after 1 h at 0°C, washed twice with 3 ml portions of ethanol and dried in air. Yield of crude product 1.1 g, corresponding to 82 % based on the pyridine complex. The product was recrystallized by dissolution in 12 ml of water at 90°C, filtration, addition of 0.5 ml 12 M hydrochloric acid, and cooling to 3°C. The ruby red crystals were washed twice with 2 ml portions of ethanol and dried. Yield 0.9 g, corresponding to 82 % of the crude product. (Found: Co 10.9; C 33.23; H 8.03; N 15.41; Cl 20.15. Calc. for [Co(C$_5$H$_{12}$N$_2$)$_3$]Cl$_3$.4H$_2$O: Co 10.96; C 33.50; H 8.25; N 15.62; Cl 19.79.) The water content was determined by thermogravimetry. 8.03 mg of the complex was heated in air with a rate of 5°C min^{-1}. Constant weight was observed from 150 − 175°C where 1.04 mg had been lost, corresponding to 3.85 mol of water per mol of cobalt. $(\varepsilon,\lambda)_{max}$: (73.4, 490); (82.0, 352). $(\varepsilon,\lambda)_{min}$: (8.0, 405); (65.0, 332). Medium: water.

Tris-*(cis-1,2-cyclopentanediamine)cobalt(III)*   *bromide*   *and*   *chloride,*   [Co(*cis*-cptn)$_3$]X$_3$.3H$_2$O. (X = Br, Cl). The chloride was prepared in a similar way as the *trans*-diamine complex from 2.9 g of *trans*-[Copy$_4$Cl$_2$]Cl.6H$_2$O (5 mmol) and 1.5 g of *cis*-1,2-cyclopentanediamine (15 mmol). The bromide was precipitated during 18 h at 3°C after addition of 0.5 g of lithium bromide and a few drops of 48 % hydrobromic acid. The crude bromide was slightly contaminated with chloride. Yields 1.2 and 0.8 g (46 % and 24 % based on pyridine complex) for the chloride and bromide, respectively. The soluble bromide and very soluble chloride were recrystallized in a similar way as the tris-*trans*-diamine complex. (Found: C 27.38; H 5.9; N 12.93; Br 36.7. Calc. for [Co-(C$_5$H$_{12}$N$_2$)$_3$]Br$_3$.3H$_2$O: C 27.53; H 6.4; N 12.88; Br 36.8.) The water content of the bromide was determined by thermogravimetry. 7.40 mg of the complex was heated in air with a rate of 5°C min^{-1}. 0.642 mg corresponding to 3.1 mol of water per mol of cobalt was lost in the range 30 − 140°C, followed by weight constancy up to 175°C.

Tris-{($\pm$)-trans-*1,2-cyclopentanediamine*}*chromium(III)*   *chloride,*   [Cr($\pm$cptn)$_3$]Cl$_3$. A mixture of 0.55 g of [Cr(DMSO)$_4$Cl$_2$]Cl.DMSO (1 mmol) and 0.30 g of ($\pm$)-*trans*-1,2-cyclopentanediamine in a stoppered test tube was heated to 80° during 40 min. After cooling to room temperature 3 ml of ethanol was added and the greyish yellow precipitate isolated by centrifugation. The product was recrystallized from 3 ml of water by dissolution at 50°C, centrifugation, and addition of 5 drops of 12 M hydrochloric acid. Yield 0.25 g, corresponding to 49 % based on DMSO complex. (Found: Cr 11.0; C 39.12; H 8.09; N 18.17; Cl 23.18. Calc. for [Cr(C$_5$H$_{12}$N$_2$)$_3$]Cl$_3$: Cr 11.09; C 39.23; H 7.91; N 18.32; Cl 23.21.) $(\varepsilon,\lambda)_{max}$: (78.6, 472); (68.5, 359). $(\varepsilon,\lambda)_{min}$: (16.0, 407); (10.5, 306). Medium: water.

Tris-*(cis-1,2-cyclopentanediamine)nickel(II)* *perchlorate,* [Ni(*cis*-cptn)$_3$](ClO$_4$)$_2$. To a solution of 0.25 g of *cis*-1,2-cyclopentanediamine (2.5 mmol) and 0.20 g of nickel(II) chloride hexahydrate (0.84 mmol) in 2 ml of water was dropwise added 1 ml of saturated sodium perchlorate solution. The blue-violet precipitate was recrystallized from water. Yield 0.35 g, corresponding to 75 % based on *cis*-cptn. (Found: Ni 10.38; C 32.25; H 6.38; N 15.05. Calc. for [Ni(C$_5$H$_{12}$N$_2$)$_3$](ClO$_4$)$_2$: Ni 10.54; C 32.28; H 6.46; N 15.07.) The magnetic susceptibility was measured by the Faraday method in the temperature range 80 − 300°K. Good agreement with Curie's law was found. $\chi_M' = 3805 \times 10^{-6}$ cgs mol^{-1} at 298°K, corresponding to $\mu_{eff} = 3.01$ BM.

Bis-*(cis-1,2-cyclopentanediamine)nickel(II)* *perchlorate,* [Ni(*cis*-cptn)$_2$](ClO$_4$)$_2$.6H$_2$O. To a solution of [Ni(*cis*-cptn)$_3$](ClO$_4$)$_2$ in water was added nickel(II) chloride and excess sodium perchlorate until the nickel-*cis*-cptn ratio was 1:2. The yellow bis-complex separated on evaporation. (Found: Ni 10.2; C 21.1; H 6.1; N 9.7. Calc. for [Ni(C$_5$H$_{12}$N$_2$)$_2$]-(ClO$_4$)$_2$.6H$_2$O: Ni 10.4; C 21.2; H 6.4; N 9.9.) Magnetic susceptibility $\chi_M' = 410 \times 10^{-6}$cgs mol^{-1} at 298°K.

trans-*Difluorobis*{($\pm$)-trans-*1,2-cyclopentanediamine*}*chromium(III)*   *perchlorate,* *trans*[Cr($\pm$cptn)F$_2$]ClO$_4$. 1.2 g of *trans*[Crpy$_4$F$_2$]ClO$_4$ (2.5 mmol), dried at 110°C for 1 h, was partially dissolved in a mixture of 0.7 g of ($\pm$)-*trans*-1,2-cyclopentanediamine (7

mmol) and 5 ml of 2-methoxyethanol. The mixture was bubbled with nitrogen and then heated in a stoppered flask to 100°C during 2 h. After cooling the pink *trans*-complex was precipitated with a 1:1 v/v ether-ethanol mixture. The product was recrystallized three times from 0.01 M perchloric acid and washed with methanol. The yield was low, approximately 0.15 g corresponding to 25 % based on the pyridine complex. (Found: Cr 12.64; C 30.02; H 6.12; N 13.70. Calc. for $[Cr(C_5H_{12}N_2)_2F_2]ClO_4.H_2O$: Cr 12.75; C 29.43; H 6.42; N 13.74.) $(\varepsilon,\lambda)_{max}$: (27.4, 504); (16.5, 408); (25.9, 349). $(\varepsilon,\lambda)_{shoulder}$: (24.7, 540); $(\varepsilon,\lambda)_{min}$: (14.7, 436); (15.3, 389); (13.8, 300).

Separation of the isomers

lel_3 and ob_3 *tris-{(−)-trans-1,2-Cyclopentanediamine}cobalt(III)* *chloride*. 0.2 g of $(+)$-$[Co(-cptn)_3]Cl_3.4H_2O$ dissolved in 25 ml of water was adsorbed on the top of a column of a SE-Sephadex C-25 cation exchanger (length 20 cm, cross section 2.5 cm²) and slowly eluted with 0.15 M disodium hydrogenphosphate. A good separation was obtained between an intensely coloured and a weakly coloured slowly moving band (approximately 90 % and 10 %, respectively). The two fractions were acidified to pH 3 with 4 M hydrochloric acid on the Sephadex column and eluted with 1 M hydrochloric acid in order to remove phosphate ions. The eluted fractions were evaporated in an evacuated desiccator with potassium hydroxide and recrystallized from water. The first fraction (90 %) was Δ-lel_3-$[Co(-cptn)_3\lambda\lambda\lambda]Cl_3.4H_2O$. $(\Delta\varepsilon,\lambda)_{extr.}$: (−0.58, 534) (+1.89, 476); (+0.32, 354). The second fraction (10 %) was Λ-ob_3-$[Co$-$(-cptn)_3\lambda\lambda\lambda]Cl_3.4H_2O$. $(\Delta\varepsilon,\lambda)_{extr.}$: (−2.95, 518); (+0.58, 458); (+0.49, 355). Both isomers have absorption spectra identical to that of $(+)$-$[Co(-cptn)_3]Cl_3$.

Single crystal CD spectrum of Δ-lel_3-$[Co(-cptn)_3\lambda\lambda\lambda]Cl_3.4H_2O$ *diluted in* Δ-lel_3-$[Rh(-chxn)_3\lambda\lambda\lambda]Cl_3.4H_2O$ (−chxn = (−)-*trans*-1,2-cyclohexanediamine). A solution of Δ-lel_3-$[Rh(-chxn)_3\lambda\lambda\lambda]Cl_3.4H_2O$ [18] and Δ-lel_3-$[Co(-cptn)_3\lambda\lambda\lambda]Cl_3.4H_2O$ in the molar ratio 100:1 was partly evaporated by standing under an inverted beaker during one week. Some of the separated pink crystals were regular hexagonal pyramids with a planar basis (approximately 5 × 5 mm) perpendicular to the c-axis. It was possible to cut these crystals along the (001) direction parallel to the basis.

Measurements were performed on crystals with a thickness of approximately 0.5 mm mounted across a hole in a metal plate on a two circle goniometer. The CD spectrum was unchanged by rotation of the crystals around the c-axis. The density of the crystals, 1.412 g cm⁻³, was calculated from the unit cell dimensions, determined from Guinier powder diagrams, and the cobalt concentration determined by atomic absorption. $(\Delta\varepsilon,\lambda)$: (−18.8, 510).

C_1- and C_3-*Tris(cis-1,2-cyclopentanediamine)cobalt(III)* *chloride*. The separation of geometrical isomers (C_1 and C_3, referring to their symmetry) was performed as described for $[Co(-cptn)_3]Cl_3$ by elution with 0.2 M disodium hydrogenphosphate. A good separation into two bands was obtained (the second fraction was the more intensely coloured). Each fraction was separated in the optical isomers on another SE-Sephadex C-25 cation exchanger by elution with a 0.20 M sodium potassium tartrate solution. (Found: Co 12.08; C 37.17; H 7.58; N 17.48. Calc. for $[Co(C_5H_{12}N_2)_3]Cl_3.H_2O$: Co 12.18; C 37.21; H. 7.85; N 17.37.) The Δ isomers of the two fractions have the CD spectra: 1. fraction $(\Delta\varepsilon,\lambda)$: (−2.60, 499); (+0.108, 425); (−0.108, 365). 2. fraction $(\Delta\varepsilon,\lambda)$: (−2.91, 491); (−0.03, 405): (−0.16, 370). The absorption spectra are identical. $(\varepsilon,\lambda)_{max}$: (110.5, 477); (104.0, 344). $(\varepsilon,\lambda)_{min}$: (12.3, 395); (47.9, 312). Medium: water.

No assignment of symmetry of the two isomers was obtained.

DISCUSSION

Preparations. Jaeger [1] prepared *trans*-1,2-cyclopentanediamine according to the following reaction scheme:
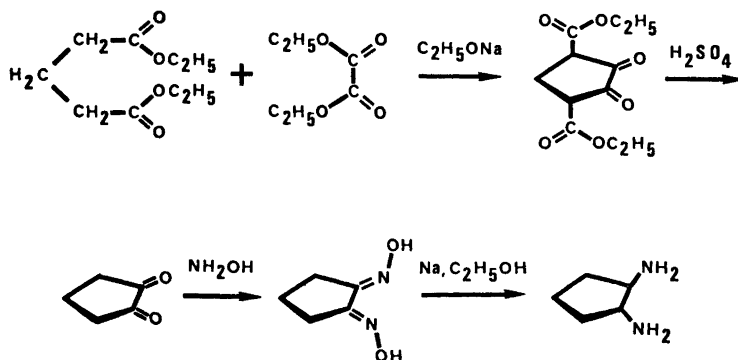
This method required the isolation of all the intermediates and was shown to be very tedious. The yield was in all cases low. A method first proposed by Cope [11] and later used by Phillips and Royer [4] has here been adapted to preparations on a larger scale.
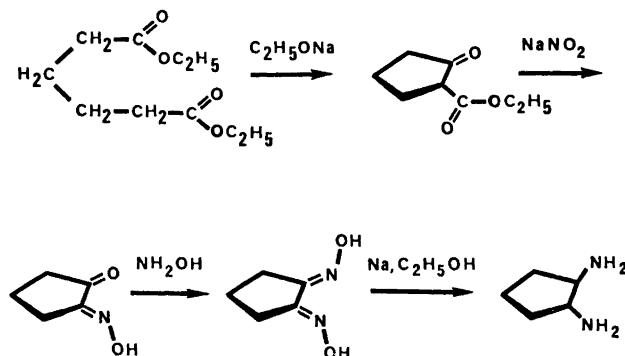
This method avoids the isolation of the unstable 1,2-cyclopentanedione. The reaction between the dione and hydroxylamine yields the *anti*-dioxime only, whereas the monoxime in the last reaction scheme gives a mixture of the *anti*- and the *amphi*-dioxime, approximately in the ratio 2:1. The *anti*-dioxime is only slightly soluble in water and gives a red bis-complex with nickel(II), whereas the *amphi*-dioxime is soluble in water and gives a yellow-brown bis-complex with nickel(II). The critical step in both reaction schemes is the reduction of the dioxime. The yield is not mentioned in Jaeger's work.[1] Our numerous experiments under different experimental conditions gave a maximum yield of 18 %.

In contrast to the dioximes both of the two bis-dioximatonickel(II) complexes were readily reduced with sodium tetrahydridoborate in "diglyme". The amine formed in this case appeared to be pure *cis*-1,2-cyclopentanediamine.

As the *cis-* and *trans*-1,2-cyclopentanediamines are readily oxidized by oxygen and hydrogen peroxide, the conventional methods of preparation of tris-diamine-cobalt(III) complexes by oxidation of cobalt(II) are unsuccessful. Thus Phillips and Royer [4] were unable to reproduce Jaeger's preparation but obtained a yield of 50 % by reacting "$Na_3[Co(CO_3)_3].3H_2O$" with the diamine. In this work we obtained an almost quantitative yield from the reaction between *trans*-[Copy$_4$Cl$_2$]Cl [6] and the diamine in 2-methoxyethanol solution. The tris-(*trans*-1,2-cyclopentanediamine)cobalt(III) chloride prepared by this method appeared to be identical to Jaeger's and Phillips' products. The complex is red, both in the crystalline state and in solution, and the crystals of the racemic chloride form triclinic pinacoids. A similar preparative procedure under anhydrous conditions gave the same complex. It was therefore anticipated that this complex was a normal tris-complex and not a dimer containing coordinated water as postulated by Phillips and Royer. The absence of coordinated water was verified by our finding that the absorption spectra were identical in acid and basic solution. The position of the low energy ligand field transition was expected to shift $5-10$ nm from the aqua- to the hydroxo-complex. Conclusive evidence is found from the crystal structure of Λ-lel$_3$-[Co($+$cptn)$_3$$\delta\delta\delta$]Cl$_3$.4H$_2$O recently published by Saito et al.[5,12]

trans-1,2-Cyclopentanediamine forms normal chelate bis- and tris-complexes with chromium(III). Thus the reaction of the diamine with [Cr(DMSO)$_4$Cl$_2$]Cl.DMSO [7] gives the orange tris-complex and with *trans*-
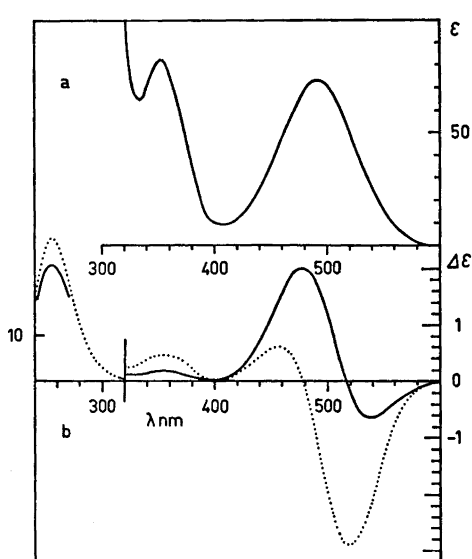

Fig. 1. a. Absorption spectrum of Δ-lel$_3$-[Co($-$cptn)$_3$]$^{3+}$. b. CD spectra of Δ-lel$_3$-[Co($-$cptn)$_3$]$^{3+}$ (————) and Λ-ob$_3$-[Co($-$cptn)$_3$]$^{3+}$ (. . . . .).
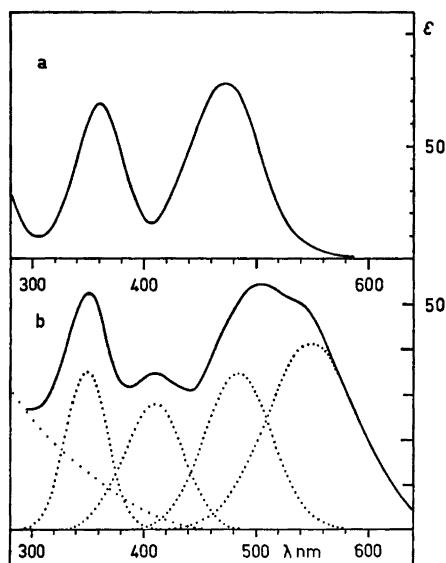
Fig. 2. a. Absorption spectrum of [Cr($\pm$cptn)$_3$]$^{3+}$. b. Absorption spectrum of *trans*-[Cr($\pm$cptn)$_2$F$_2$]$^+$ and its resolution into Gaussian components.

$[Copy_4F_2]ClO_4$ [8] it gives pink *trans*-difluoro-bis-complex. Both complexes are more labile than other Co(III) and Cr(III) diamine complexes. The yields of these reactions are lower than for similar diamines, probably partly due to oxidation of the diamine.

The tris-(*cis*-1,2-cyclopentanediamine)cobalt(III) complex was prepared in the same way as the *trans*-diamine complex but resembles other tris-diamine complexes in that it has a similar absorption spectrum and is less labile than the *trans*-diamine complex. This would be expected for steric reasons.

Absorption spectra. Absorption spectra in aqueous solution are shown for $[Co(\pm cptn)_3]^{3+}$ and $[Co(cis\text{-}cptn)_3]^{3+}$ in Figs. 1a and 3a, respectively, and for $[Cr(\pm cptn)_3]^{3+}$ and *trans*-$[Cr(\pm cptn)_2F_2]^+$ in Figs. 2a and 2b, respectively.
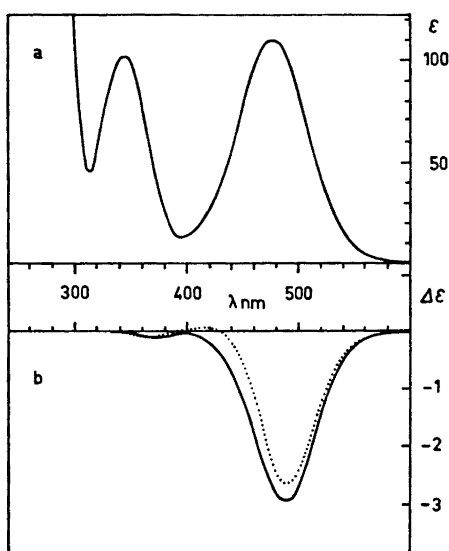
Fig. 3. a. Absorption spectrum of Δ-$[Co(cis\text{-}cptn)_3]^{3+}$. b. CD spectra of the 1st (———) and 2nd (.....) fraction of Δ-$[Co(cis\text{-}cptn)_3]^{3+}$.

The positions of the two ligand field absorption bands of the tris-complexes together with calculated values of the ligand field parameter Δ and the Racah interelectronic repulsion parameter B are tabulated in Table 1. For the d^6 complexes the calculations are based on the assumption of octahedral sym-

Table 1. Positions of ligand field absorption bands in kK.

	1. band	2. band	Δ	B
$[Co(tr\text{-}cptn)_3]^{3+}$	20.41	28.33	21.38	0.577
$[Co(cis\text{-}cptn)_3]^{3+}$	21.01	29.16	22.01	0.593
$[Co\ en_3]^{3+}$	21.50	29.50	23.30	0.590
$[Cr(tr\text{-}cptn)_3]^{3+}$	21.19	27.86	21.19	0.627
$[Cr\ en_3]^{3+}$	21.90	28.60	21.90	0.627

metry, the Racah parameter $C = 4B$, and the approximate expressions given by C. K. Jørgensen.[13a] For the d^3 complexes $\varDelta$ is taken directly from the position of the low energy absorption band and B from the appropriate secular determinant.[13b]

Until the publication [5] of the complete X-ray crystal structure of $\varLambda$-lel$_3$-[Co(+cptn)$_3\delta\delta\delta$]Cl$_3$.4H$_2$O by Saito *et al.* we believed that the small value of $\varDelta$ in the cptn-complexes could be explained [14] by pronounced deviation from 90° of the N$-$Co$-$N angle because of strain induced by the nearly planar cyclopentane ring. Saito's work, however, shows that this angle is very close to the angle found in ethylenediamine complexes. That other factors are significant is also seen from the fact that in the probably strain free *cis*-cptn cobalt complex the value of $\varDelta$ is relatively low.

The absorption spectrum of [Cr($\pm$cptn)$_3$]$^{3+}$ is, however, more similar to other tris-diaminechromium spectra.

Isomers of [Co(cptn)$_3$]$^{3+}$. The experiments of Jaeger [1] seemed to indicate that the formation of [Co($\pm$cptn)$_3$]$^{3+}$ was stereospecific. Of the eight possible isomers he obtained only two, each containing only $+$cptn or $-$cptn. These were probably mixtures containing $\varLambda$-lel$_3$- and $\varDelta$-ob$_3$-[Co($+$cptn)$_3$]$^{3+}$ and $\varDelta$-lel$_3$- and $\varLambda$-ob$_3$-[Co($-$cptn)$_3$]$^{3+}$, respectively. Corey and Bailar [15] tried to explain why Jaeger observed only one component in each fraction by suggesting that the ob$_3$-isomers were unstable compared to the lel$_3$-isomers. Their conformational analysis showed, however, this energy difference to be small (1.8 kcal/mol). At equilibrium this corresponds to the presence of approximately 5 % of the ob$_3$-isomer.[4]

We actually succeeded in separating the [Co($-$cptn)$_3$]$^{3+}$ complex, prepared from $-$cptn and *trans*-[Copy$_4$Cl$_2$]Cl, into two well separated fractions on an SE Sephadex C-25 cation exchanger by elution with 0.15 M HPO$_4{}^{2-}$. The first fraction, estimated to be about 90 % of the total amount, was from the CD-spectrum assumed to be $\varDelta$-lel$_3$-[Co($-$cptn)$_3$]$^{3+}$. This is in agreement with Gillard's suggestion,[16,17] based upon the ORD-spectrum measured by Jeager. The assumption has been verified by the determination of the absolute con-
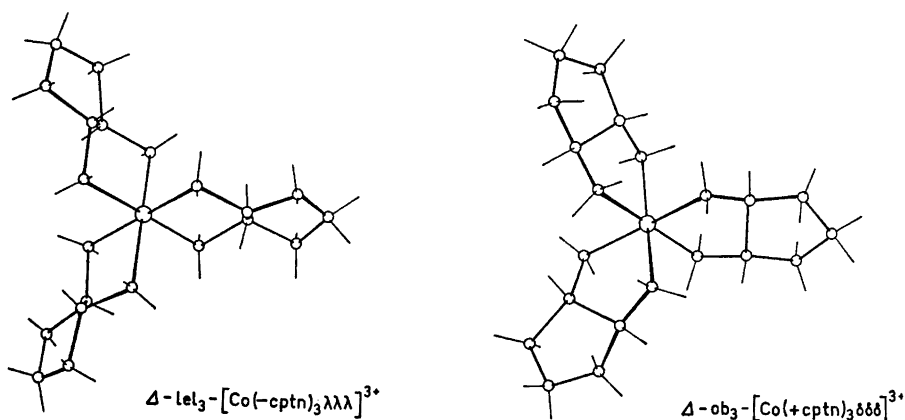

Fig. 4. $\varDelta$-lel$_3$ and $\varDelta$-ob$_3$ isomers of [Co(*trans*-cptn)$_3$]$^{3+}$ viewed along the 3-fold axis.

figuration.[5] The CD-spectrum of Λ-lel$_3$-[Co(+ cptn)$_3$]$^{3+}$ in aqueous solution [5] is the mirror image of our spectrum of Δ-lel$_3$-[Co(− cptn)$_3$]$^{3+}$. This CD-spectrum (Fig. 1b) is unusual in having intensity ratios of the A_2- and E-components of the low energy ligand field band opposite to those of Δ-lel$_3$-[Co(− chxn)$_3$]$^{3+}$ and Δ-[Coen$_3$]$^{3+}$. It is worthy of note that the CD-spectrum of the powder in a potassium bromide matrix has the usual intensity ratio (Fig. 5). The purity
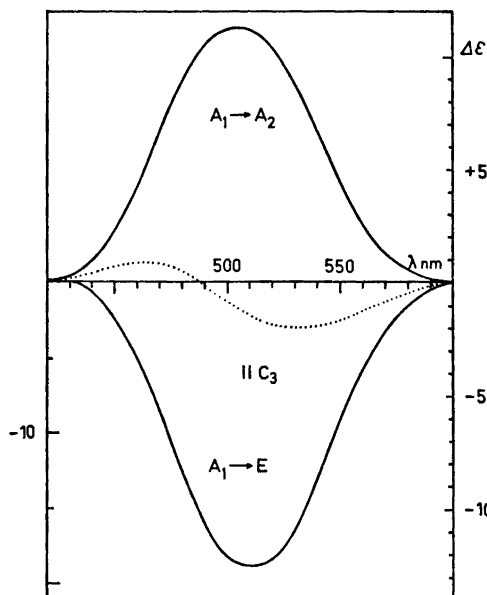

Fig. 5. Single crystal CD spectrum of Δ-lel$_3$-[Co(− cptn)$_3$]Cl$_3$.4H$_2$O, diluted in Δ-lel$_3$-[Rh(− chxn)$_3$]Cl$_3$.4H$_2$O with light propagating along the cryst. c-axis. (————, negative, left hand ordinate). The right hand ordinate is reduced by a factor of $\frac{2}{3}$, corresponding to a random orientation, comparable to the powder potassium bromide disc spectrum (. . . . ., right hand ordinate). The positive band (————, right hand ordinate) is the $A_1 \rightarrow A_2$ component predicted from Gaussian analysis.[22]

of our resolved cptn allowed us to conclude that the second fraction was Λ-ob$_3$-[Co(− cptn)$_3$]$^{3+}$. [The CD-spectrum of this isomer (Fig. 1b) is completely different from the spectrum of Λ-ob$_3$-[Co(− chxn)$_3$]$^{3+}$. The − chxn complex shows only a single positive deflection at 500 nm.[21] This, therefore, is a case where the assignment of the absolute configuration from the CD-spectrum seems impossible. We tried to reestablish equilibrium from both directions between the lel$_3$ and ob$_3$ isomers by treatment with activated carbon. However, because of decomposition of the complexes, this was impossible.

Single crystal CD-spectrum. Δ-lel$_3$-[Co(− cptn)$_3$]Cl$_3$.4H$_2$O crystallizes in the hexagonal space group $P6_122$. Saito *et al.*[12] showed that the molecular pseudo threefold axis deviates approximately 22° from the c-axis. We found that Δ-lel$_3$-[Co(− cptn)$_3$]Cl$_3$.4H$_2$O was able to syncrystallize with Δ-lel$_3$-[Rh(− chxn)$_3$]Cl$_3$.4H$_2$O [18] ($P6_122$). We assume that this rhodium complex just as Δ-lel$_3$-[Co(− chxn)$_3$]Cl$_3$.4H$_2$O [19] has a much smaller angle between the pseudo threefold and the c-axis.

The CD-spectrum was recorded along the c-axis. It showed a single negative deflection at 510 nm with $\Delta\varepsilon = -18.8$ (Fig. 5). In this orientation the only

allowed transition is $A_1 \to E$. It is therefore concluded that the low energy component of the red ligand field band is an $A_1 \to E$ transition. In Fig. 5 the crystal CD-spectrum is shown, reduced by a factor of 2/3 corresponding to random orientation, and compared to the powder potassium bromide disc spectrum. The position of the $A_1 \to A_2$ component was estimated from the difference between the two spectra. The A_2 and E components are separated by approximately 240 cm^{-1}.

The solid state and solution spectra are not directly comparable, probably because of different conformations in the two media.

Isomers of [Co(cis-*cptn*)$_3$]$^{3+}$. The [Co(*cis*-cptn)$_3$]$^{3+}$ ion may consist of four isomers. Each pair of enantiomers are characterized by having the cyclopentane rings placed so that the molecule has either C_3 or C_1 symmetry (Fig. 6).
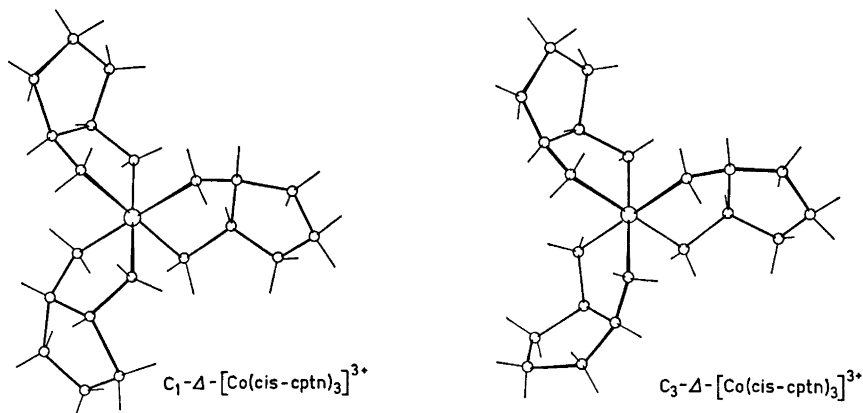

Fig. 6. The C_1 and C_3 isomers of Δ-[Co(*cis*-cptn)$_3$]$^{3+}$ viewed along the pseudo 3-fold axis.

The geometrical isomers were separated on SE-Sephadex C-25 cation exchanger by elution with a 0.2 M sodium hydrogenphosphate solution, followed by optical resolution of each pair on the same ion exchanger by elution with a 0.2 M tartrate solution. Our product contained approximately equal amounts of the C_1 and C_3 isomers, having identical absorption spectra. The CD-spectra of the two geometrical isomers with the same absolute configuration are very similar (Fig. 3b). This was expected as the nearest coordination spheres of the two isomers are almost identical. No identification of the two isomers was easily available from the NMR-spectra.

In contrast to $\pm$ cptn, *cis*-cptn with Ni(II) forms a yellow bis-complex which was precipitated as the perchlorate salt. The magnetic susceptibility of this complex is $\chi_M{}' = +410 \times 10^{-6}$ cgs mol^{-1} (25°C). Similar properties are found in the bis-complex of *meso*-2,3-butanediamine.[20] By addition of excess of *cis*-cptn, a blue tris-complex was formed and precipitated as the perchlorate salt. This complex has the expected paramagnetism. $\chi_M{}' = 3800 \times 10^{-6}$ cgs mol^{-1} at 25°C.

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