

## Preparation and Chromatographic Separation of Diastereoisomeric Ions of Tris[(*R*)-1-phenyl-1,2-ethanediamine]cobalt(III)

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Racemic 1-phenyl-1,2-ethanediamine has been prepared and resolved in its catoptric forms. The (–)<sub>D</sub>-*R* isomer was used in preparation of the tris-[(*R*)-1-phenyl-1,2-ethanediamine]cobalt(III) cation of which four diastereoisomers are expected to form. By means of chromatography on Sephadex SP-C25 the diastereoisomers have been separated and three of them have been isolated and characterized by their visible–UV absorption and circular dichroism spectra and <sup>1</sup>H NMR spectroscopy. It is shown that the *meridional* *le*<sub>3</sub> and *facial* *le*<sub>3</sub> forms have different circular dichroism spectra.

Since Werner's work on optically active cobalt(III) complexes the tris-diamine cobalt(III) complexes have been the subject of very detailed investigations in order to unravel the connection between the chiroptical properties and the varied configurational and conformational structures. In this respect the tris(1,2-propanediamine)cobalt(III) complexes, [Co(pn)<sub>3</sub>]<sup>3+</sup>, have played an important role in clarifying our understanding of the stereochemistry and also in developing experimental techniques to separate and characterize the altogether 24 different cations. One of these isomers was characterized by X-ray diffraction to be the *fac*-Δ-[Co(*R*-pn)<sub>3</sub>]<sup>3+</sup>.<sup>1</sup> At this time it had already been realized<sup>2</sup> that the synthetic route could yield a mixture of the *fac* and *mer* isomers of Δ-[Co(*R*-pn)<sub>3</sub>]<sup>3+</sup>. The crystal structure determination was made from the bulk crystalline material of a preparation and from considerations about the statistical ratio of the *fac* and *mer* geometric isomers this sample was expected to contain about three times more of the *mer* isomer than of the *fac* isomer. It was noted that a single crystal taken from a batch was not necessarily

representative of the whole batch.<sup>3</sup> MacDermott<sup>4,5</sup> succeeded in separating the geometric isomers of Δ-[Co(*R*-pn)<sub>3</sub>]<sup>3+</sup> after having realized that the bromide of the *fac* form but not that of the *mer* isomer is crystalline. After precipitating the *fac* bromide the *mer* form could be isolated as the crystalline dithionate.

The chromatographic separation on Sephadex of the *fac* and *mer* Δ-[Co(*R*-pn)<sub>3</sub>]<sup>3+</sup> isomers was achieved much later and an extensive study of the isomer distribution of [Co(pn)<sub>3</sub>]<sup>3+</sup> was reported by Harnung *et al.*<sup>6</sup> In these investigations and in similar studies (*e.g.* Ref. 7) it was found that the absorption and circular dichroism spectra of *fac* and *mer* pairs of isomers were nearly if not totally indistinguishable. If this result is general it means that a theoretical model for optical activity of these complexes need only be concerned with the spatial distribution of the nearest and next nearest neighbouring atoms to the central metal ions. The present work was started to test this point with complexes of a ligand considered more unsymmetric than 1,2-propanediamin, *i.e.* 1-phenyl-1,2-ethanediamine (phenen). The ligand is not commercially available but obtainable from acetophenone by a synthetic route which is convenient only for rather small amounts. Therefore the investigation was restricted to the four tris complexes formed by (–)<sub>D</sub>-1-phenyl-1,2-ethanediamine: (*fac* or *mer*)-(Δ or Λ)-[Co((–)<sub>D</sub>-phenen)<sub>3</sub>]<sup>3+</sup>. This system has been studied<sup>8</sup> to some extent previous to the development of conformational analysis of chelate rings and therefore not with the same intentions as ours.

## EXPERIMENTAL

*Physical measurements.* Absorption spectra were recorded on a Cary 118 spectrophotometer and circular dichroism on a Roussel-Jouan Dichrographe IIIS.  $^1\text{H}$  NMR spectra were obtained on a Bruker HX-270 spectrometer. A Perkin-Elmer AA 305 was used for atomic absorption analyses.

## Preparations

*Isonitrosoacetophenone* was prepared by Claisen condensation from acetophenone and butylnitride added to sodium ethanolate in ethanol.

*Phenylglyoxime*<sup>9</sup> was obtained from isonitrosoacetophenone (100 g) in 150 ml of water to which was added 500 ml of ethanol, 100 g hydroxylammonium chloride, 170 ml 6 M acetic acid and 25 g of sodium acetate. The mixture was refluxed for 2 h and then left to cool to room temperature. Crystallization of the desired product was initiated by scratching. Yield 48 g (~45%).

*Phenylethylenediamonium chloride.* 44 g of phenylglyoxime dissolved in 1 l of absolute ethanol was reduced with *ca.* 130 g sodium. After cooling, first 100 ml 4 M hydrochloric acid then excess 12 M hydrochloric acid were added. After filtration the red solution was evaporated to 400 ml and again filtered. The pH of the filtrate was adjusted to 3–4 with 2 M sodium hydroxide and to this solution was added 90 g of wet picric acid dissolved in 1 l of boiling water. After cooling to room temperature the picrate was filtered, washed with water and then suspended in 300 ml of water. Picric acid was liberated and to a large extent removed by filtration after the addition of 300 ml of 12 M hydrochloric acid. The yellow filtrate was evaporated to near dryness. The addition of 300 ml of ethanol dissolved the remaining picric acid and precipitated most of the amine as the hydrochloride. The product was washed with ether or acetone. Characteristic yield 25–30 g (45–55%).

*Resolution of racemic phenen.2HCl.*<sup>10</sup> 33.3 g (0.154 mol) phenen.2HCl was dissolved in 200 ml of water. The solution was placed on a column of IRA-402 anion exchanger in the  $\text{OH}^-$  form (length 35 cm, diameter 7.5 cm) and eluted with water. The basic part of the eluate was collected and to this was added 23.0 g (0.154 mol) of (+)<sub>D</sub>-tartaric acid. The volume of the solution was then reduced until precipitation commenced. Thereafter the resolving procedure of Reilen *et al.*<sup>10</sup> was followed.

$[\text{Co}((-)_D\text{-phenen})_3]\text{Cl}_3$ . The complex was prepared by the method analogous to that of Michelsen.<sup>11</sup> 3 g (10.5 mmol) (-)<sub>D</sub>-phenylethylenediamonium (+)<sub>D</sub>-tartrate was added to a solution of 0.81 g (19.2 mmol)  $\text{LiOH}\cdot\text{H}_2\text{O}$  in 8 ml of hot water.

The solution was cooled in an ice bath and 20 ml of ethanol and later 30 ml pyridine were added. After removal of the lithium tartrate by filtration the filtrate was poured into a suspension of 1.5 g (2.54 mmol) *trans*-dichloridotetrapyridinecobalt(III) chloride hexahydrate in 30 ml of pyridine. The mixture was stirred for 20 min at room temperature and then evaporated to dryness. The yellow product was kept evacuated over sulfuric acid for 24 h to remove most pyridine.

*Chromatographic separation of diastereoisomers.* 7 g of the crude product was dissolved in 500 ml 0.1 M sodium perchlorate at 60–70 °C and approximately 45 ml swollen Sephadex SP-C25 was added under stirring. The slurry of the ion exchange material was placed on top of a column of the same material (35 cm long, 7.5 cm diameter). The column was eluted with 0.2 M sodium perchlorate. A number of red bands moved relatively fast down the column leaving an orange band on the top. This band separated slowly into four bands, in the following denoted A, B, C, D in order of their increasing elution time on the Sephadex. The first two were eluted from the column whereas the latter two bands were separated by removing the Sephadex from the top and placing each coloured fraction on a smaller column. The complex was then liberated from the Sephadex ion exchanger with 1 M hydrochloric acid. The complexes from the various fractions were each concentrated on a weak cation exchange resin (Bio-Rex 70) and eluted with 0.1 M hydrochloric acid. From the eluates the slightly soluble perchlorates were precipitated by addition of a 5 M sodium perchlorate solution. In this way pure samples of the diastereoisomers from band A, C, and D were isolated. Band B was the least intensely coloured band and it was not completely separated from band A. Therefore, the amount of complex in the fraction considered to contain only the compound B was small and not enough was isolated to allow both analysis and characterization of the complex.

Similar chromatographic separations on a smaller scale were used to compare the relative amounts of cobalt(III) complex in each band by absorption spectroscopy. Analysis C, H, N, Cl, Co.

## Equilibrium studies

A few experiments were performed in order to establish equilibrium between the diastereoisomers of  $[\text{Co}((-)_D\text{-phenen})_3]^{3+}$ . A typical example is: 0.805 g (1.0 mmol) of the diastereoisomer from band C (demonstrated to be  $\Delta$ -*mer*- $[\text{Co}(R\text{-phenen})_3](\text{ClO}_4)_3\cdot 2\text{H}_2\text{O}$  (*vide infra*), 0.160 g (1.2 mmol) (-)<sub>D</sub>-phenen and 70 mg charcoal (Norit W) were added to 125 ml of water. The pH was

adjusted to 7.0 by addition of 1 M perchloric acid. Under a slow nitrogen flow the mixture was stirred at 60 °C for 48 h. The charcoal was removed by filtration and the solution was analysed by the above-mentioned chromatographic technique. The amount of complex in each band was measured by absorption and atomic absorption spectroscopy.

## RESULTS AND DISCUSSION

Tris{(-)<sub>D</sub>-1-phenyl-1,2-ethanediamine}cobalt(III) chloride, [Co((-)<sub>D</sub>-phenen)<sub>3</sub>]Cl<sub>3</sub>, has been prepared from *trans*-dichloridotetrapyridinocobalt(III) chloride and (-)<sub>D</sub>-phenen as the (+)<sub>D</sub>-tartrate in pyridine. The resulting crude material was separated into four diastereoisomers (A, B, C, and D in order of increasing elution time) by ion exchange chromatography on Sephadex SP-C25. The preparative route need not give an isomer distribution close to that determined by the relative stabilities of the isomers. However, it was found that pure samples of isomer C (or A or D) in the presence of the free ligand and activated charcoal could equilibrate at 60 °C during 48 h to the same relative mixture of diastereoisomers. Different independent preparations and equilibrated samples gave the relative amounts A:B:C:D = 0.26:0.05:2.9:1.0. The very small amounts of fraction B present prevented us from isolating enough of this isomer for its characterization. The three isomers A, C, and D have identical or nearly identical absorption spectra in the visible and ultraviolet region. The first spin allowed band has maximum at 468 nm ( $\epsilon = 126$ ). The second band is only observed as a shoulder due to the rising absorption from the phenyl group (Fig. 1).

The circular dichroism spectra of the diastereoisomers A, C, and D are shown in Fig. 1. The CD spectrum of A consists of a single component under the first absorption band with its maximum approximately coinciding with that of the absorption. This kind of behaviour has often been noticed (see, e.g., Ref. 6) for tris( $\alpha,\beta$ -diamine)cobalt(III) complexes but only for ob<sub>3</sub> complexes. The CD spectra of C and D are also typical, however, for le<sub>3</sub> complexes. The observed signs for the Cotton effects under the first absorption band dictate the absolute configuration of the cations and from the knowledge<sup>12</sup> that the absolute configuration of (-)<sub>D</sub>-phenen is *R*, it follows that A is  $\Lambda$ -( $\lambda\lambda\lambda$ )-ob<sub>3</sub>- and C and D are  $\Delta$ -( $\lambda\lambda\lambda$ )-le<sub>3</sub>-[Co(*R*-phenen)<sub>3</sub>]<sup>3+</sup>. The assignment is completed by using the approximate 3:1 ratio found between the isomers A:B and C:D, re-

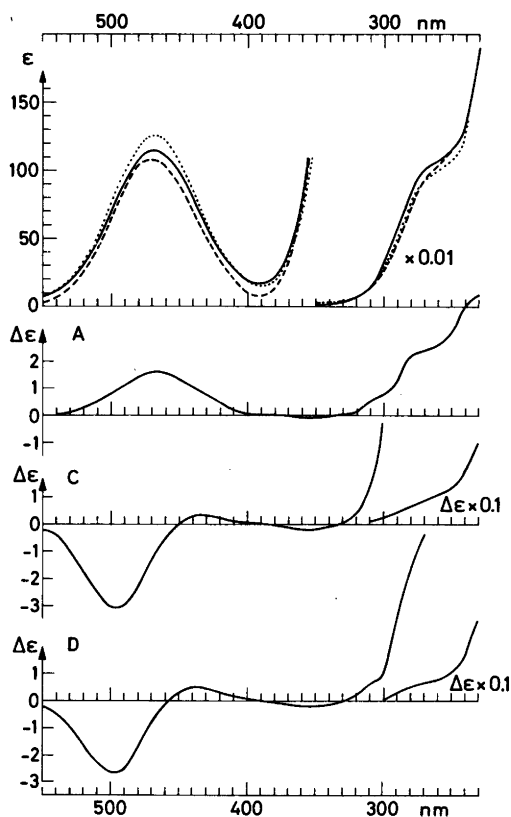


Fig. 1. Absorption spectra of *mer*- $\Lambda$ -ob<sub>3</sub>-, ...; *mer*- $\Delta$ -le<sub>3</sub>-, —; and *fac*- $\Delta$ -le<sub>3</sub>-[Co((-)<sub>D</sub>-phenen)<sub>3</sub>](ClO<sub>4</sub>)<sub>3</sub>-, ---. A, C, and D are the circular dichroism spectra of the same isomers.

spectively. This is the ratio expected between *mer*:*fac* geometric isomers. The perchlorate of isomer C was found to be a relatively insoluble material albeit a glass as judged from the absence of lines in the X-ray powder photographs. Isomer D is more insoluble and crystalline. In view of MacDermott's experiences with the corresponding isomer of tris(1,2-propanediamine)cobalt(III) bromide this information was taken as further evidence for the assignment  $\Delta$ -le<sub>3</sub>-*mer*[Co(*R*-phenen)<sub>3</sub>]<sup>3+</sup> for band C.

The assignment was finally tested with <sup>1</sup>H NMR spectroscopy. Spectra of the *N*-deuterated diastereoisomers as perchlorates in dimethyl sulfoxide-*d*<sub>6</sub> were recorded at 270 MHz. The spectrum originating from band D was clearly more simple than those of the bands A and C demonstrating the presence of a molecular three-fold axis of symmetry in D but

not in A and C. The coupling constants for the protons of isomer D were determined. The *geminal* and the *trans* coupling constants are both 13 Hz and the remaining *vicinal* coupling constant is 4 Hz. These values show that the phenyl group indeed is an equatorial substituent of the chelate ring as expected and not an axial substituent as has been detected<sup>13</sup> in a Schiff base complex of nickel(II).

Having assigned the structure of each of the found diastereoisomers we can now discuss the question of similarity between two geometric isomers, namely the *fac*- and *mer*- $\Delta$ -[Co(R-phenen)<sub>3</sub>]<sup>3+</sup>. The circular dichroism spectra shown in Fig. 1 clearly demonstrate a qualitative similarity between the CD of the two isomers. The first CD maximum falls at 497 nm for the *fac* isomer and at 496 nm for the *mer* isomer. However, the intensities,  $\Delta\epsilon$ , are widely different: -2.68 and -3.11, respectively, for the two. The second CD component under the first absorption band (at 435 nm *mer*, and at 433 nm *fac*) is more intense ( $\Delta\epsilon=0.49$ ) for the *fac* isomer than for the *mer* isomer ( $\Delta\epsilon=0.33$ ) whereas the CD band under the second spin allowed octahedral transition falls at 355 nm for both isomers and the intensities are the same within approx. 10%. We feel that these findings are important for testing theoretical models for introducing rotatory strengths in *d-d* transitions. A simple "ligating atom displacement" model seems for example to be unable to explain the observed difference in rotatory strengths while other models may prove more successful.

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