

# Geometric and Optical Isomerism in Cobalt(III) and Chromium(III) Tris Complexes of *cis*-1,2-Cyclohexanediamine

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The tris *cis*-1,2-cyclohexanediamine complexes of cobalt(III) and chromium(III) have been prepared and the four possible isomers *mer-Δ*, *mer-Λ*, *fac-Δ* and *fac-Λ* have been isolated and characterized. The equilibrium between the isomers of the cobalt(III) complex has been established at 90 °C. The identification of the isomers have been performed on the basis of the electronic, the circular dichroism, ESR and <sup>13</sup>C NMR spectra.

When a bidentate ligand, with two dissymmetric centers of opposite chirality (*R,S*) and a mirror plane as *cis*-1,2-cyclohexanediamine, (*cis*-chxn), coordinates as part of a tris complex, geometric isomers are possible for each optical enantiomers. Tris complexes with three such ligands are named *facial* (*fac*) and *meridional* (*mer*) referring to the spatial arrangement of the dissymmetric centers. The possibility of this type of isomerism has been mentioned by Woldbye<sup>1,2</sup> and Tapscott.<sup>3</sup> The first detection and separation of *fac* and *mer* isomers was performed by Toftlund and Pedersen.<sup>4</sup> The tris(*meso*-2,3-butanediamine) cobalt(III) and tris(*meso*-2,4-pentanediamine) cobalt(III) complexes have been separated in the four possible isomers by Kojima *et al.*<sup>5,6</sup> In the present paper separation and characterization of the four isomers for both [Co(*cis*-chxn)<sub>3</sub>]<sup>3+</sup> and [Cr(*cis*-chxn)<sub>3</sub>]<sup>3+</sup> will be presented. The designation of configuration is, in accordance with IUPAC,<sup>7</sup> based upon the edges of the octahedron spanned by the chelate rings. The three pairs of edges form three pairs of skew lines describing screws of the same type, either right-handed (*Δ*) or left-handed (*Λ*).

Each chelate ring may exist in one of two conformations designated as *tel* or *ob*, depending on whether the C—C bond in the chelate ring is almost parallel or oblique to the (pseudo) three-fold axis (Fig. 1).

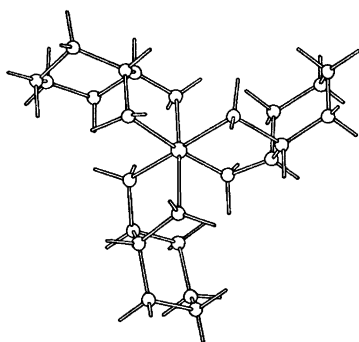
## EXPERIMENTAL

### Preparations

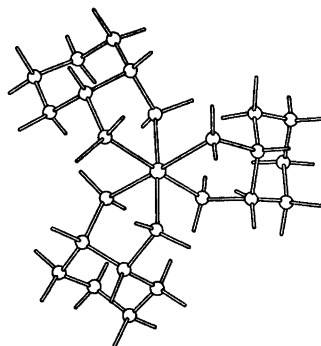
*cis*-1,2-Cyclohexanediamine. The starting material, purchased from Wolf and Kaaber Farum, contains 51 % of *trans*-, 48 % of *cis*-1,2-cyclohexanediamine and 1 % of 1,6-hexanediamine. The *trans*-1,2-cyclohexanediamine ( $\pm$  chxn) was resolved from the crude diamine (240 ml, 2.0 mol) according to Galsbøl *et al.*<sup>8</sup> The residue after removal of (–)chxn and (+)chxn, contained *ca.* 90 % *cis*-chxn and *ca.* 10 % *trans*-chxn. This residue was heated to 80 °C, and dropwise addition of sulfuric acid (60 ml 9 M) with stirring and cooling precipitated *cis*-chxn.H<sub>2</sub>SO<sub>4</sub> (46 g). The crystals were filtered off and dropwise addition of ethanol (150 ml) to the filtrate precipitated 30 g more. No *trans*-chxn could be detected by <sup>1</sup>H NMR in this product.

The *cis*-chxn was liberated from *cis*-chxn.H<sub>2</sub>SO<sub>4</sub> (73 g) with potassium hydroxide according to Galsbøl *et al.*<sup>8</sup> The diamine was distilled under nitrogen. Yield 26 g (11 % from the crude amine), b.p. 58–60 °C/1 Torr, m.p. 6 °C.

*Tris*(*cis*-1,2-cyclohexanediamine)cobalt(III) chloride [Co(*cis*-chxn)<sub>3</sub>]Cl<sub>3</sub>. To a solution of *trans*-[Copy<sub>4</sub>Cl<sub>2</sub>]Cl<sub>6</sub>H<sub>2</sub>O (8 g 13.3 mmol) in 2-methoxyethanol (25 ml) was dropwise added *cis*-1,2-cyclohexanediamine (5 g 43.8 mmol) at 25 °C. After addition of lithium chloride, (3 g) a few drops of conc. hydrochloric acid and a 1:1 v/v mixture of absolute ethanol and ether (10 ml) the orange chloride precipitated during 3 h at 0 °C. The tris complex was filtered off

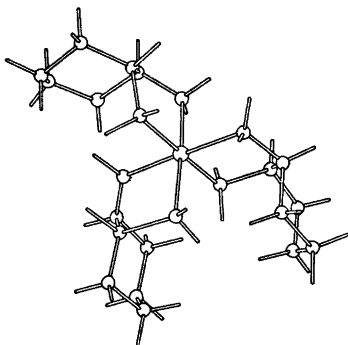


fac- $\Delta$ - $lel_3$ -[Co(cis-chxn) $_3$ ] $^{3+}$

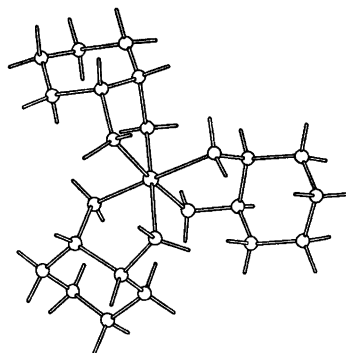


fac- $\Delta$ - $ob_3$ -[Co(cis-chxn) $_3$ ] $^{3+}$

Fig. 1a and 1b. The  $lel_3$  and  $ob_3$  conformers of  $fac-\Delta$ -[Co(cis-chxn) $_3$ ] $^{3+}$  viewed along the 3-fold axis



mer- $\Delta$ - $lel_3$ -[Co(cis-chxn) $_3$ ] $^{3+}$



mer- $\Delta$ - $ob_3$ -[Co(cis-chxn) $_3$ ] $^{3+}$

Fig. 1c and 1d. The  $lel_3$  and  $ob_3$  conformers of  $mer-\Delta$ -[Co(cis-chxn) $_3$ ] $^{3+}$  viewed along the pseudo-3-fold axis.

and washed twice with 8 ml portions of a 1:1 v/v mixture of abs. ethanol and ether. Yield: 6.3 g (93 %).

*Tris(cis-1,2-cyclohexanediamine)chromium(III) chloride*, [Cr(cis-chxn) $_3$ ]Cl $_3$ . *cis*-1,2-Cyclohexanediamine (5 g, 44 mmol) and trichlorotris(pyridine)chromium(III) (3.5 g, 8.8 mmol) was added to absolute ethanol (50 ml) (dried over molecular sieves) in a 250 ml flask provided with a reflux condenser fitted with a KOH-tube. The mixture was refluxed for 24 h. After 2 h precipitation of yellow-orange crystals commenced. The solution was filtered and the precipitate was washed twice with absolute ethanol. Yield 3.6 g (82 %) of crude [Cr(cis-chxn) $_3$ ]Cl $_3$ .

#### Separation of the isomers

*mer- and fac-Tris(cis-1,2-cyclohexanediamine)cobalt(III) bromide and perchlorate.* Separation

of the isomers was done on SP-Sephadex C-25 cation exchange resin using 0.19 M potassium sodium (+)-tartrate as an eluent. A good separation into three bands was obtained; 1. *mer-A* 2. *mer-A-fac-A* and 3. *fac-A*. The three fractions were diluted, resorbed on new columns, washed with water and eluted with 0.5 M sodium perchlorate (1st fraction) or with 1 M lithium bromide (2nd and 3rd fractions). The eluates were concentrated by evaporation on a vacuum rotary evaporator and by cooling in ice the complex salts precipitated as orange crystals. The products were reprecipitated from water with saturated sodium perchlorate or saturated sodium bromide. From 1.0 g crude [Co(cis-chxn) $_3$ ]Cl $_3$  we obtained 0.31 g (1st fraction *ca.* 30 %) of *mer-A*. {Anal. [Co(C $_6$ H $_{14}$ N $_2$ ) $_3$ ](ClO $_4$ ) $_3$ : Co, C, H, N, Cl} and 0.20 g (3rd fraction *ca.* 20 %) of *fac-A*. Anal. [Co(C $_6$ H $_{14}$ N $_2$ ) $_3$ ]Br $_3$ ·2H $_2$ O: Co, C, H, N, Br. *mer- and fac-Tris(cis-1,2-cyclohexanediamine)chromium(III) perchlorate.* Separation of

the *facial* and *meridional* isomers was done on SP-Sephadex C-25 cation exchange resin using 0.15 M disodium hydrogenphosphate as an eluent.

The *facial* and *meridional* isomers were resorbed on a new column and separated into their optical enantiomers using 0.2 M disodium tartrate. Finally all four isomers were resorbed on a new column and eluted with 0.5 M sodium perchlorate; the eluates were concentrated by evaporation on a vacuum rotary evaporator, whereby most of the complexes separated as yellow crystals. All separations were performed in the dark at 5 °C to prevent hydrolysis.

The products were reprecipitated from water with 60 % perchloric acid. From 2.0 g crude  $[\text{Cr}(\text{cis-chxn})_3]\text{Cl}_3$  we obtained 0.50 g of each of the *facial* enantiomers and 0.15 g of each of the *meridional* ones. Anal.  $[\text{Cr}(\text{C}_6\text{H}_{14}\text{N}_2)_3](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ ; Cr, C, H, N, Cl.

*Determination of the relative equilibrium constants.* *fac*- $[\text{Co}(\text{cis-chxn})_3]^{3+}$  (100 mg, 0.7 mmol) was dissolved in water (10 ml). *cis*-chxn.2HCl (17.5 mg, 0.1 mmol) was added and pH was adjusted to 7 with 0.1 M sodium hydroxide. Charcoal (Medicinsk A, Struers) (10 mg) was added and the mixture was heated to 90 °C. The mixture was stirred mechanically and the temperature was kept constant for 15 min. The equilibrium was quenched with 0.1 M HCl (4 ml) and the mixture was filtered. After dilution to 100 ml the *fac* and *mer* isomers were separated on an SP-Sephadex-C-25 cation exchanger by elution with a 0.25 M sodium (+)-tartratoantimonate (III) solution and the contents of cobalt were measured in each fraction by atomic absorption.

## Measurements

Absorption and circular dichroism spectra were measured with a Cary 14 Spectrophotometer and a Jouan Dichrographe 2B. The cobalt(III) and chromium(III) concentrations were determined by atomic absorption with a Beckman 1248 Atomic Absorption Spectrophotometer. Proton-decoupled 15.03 MHz  $^{13}\text{C}$  NMR spectra were measured with a JEOL FX-60 NMR Spectrometer. The ESR measurements were done at 9.115 GHz using a JEOL JES-ME-IX spectrometer.

## RESULTS AND DISCUSSIONS

*Preparations.* As the *cis*-1,2-cyclohexanediamine is a rather poor ligand, the conventional method of preparation of *tris*-diamine-cobalt(III) complexes by oxidation of a cobalt(II) diamine mixture with molecular oxygen was unsuccessful. Instead we obtained an almost quantitative yield from the reaction

between *trans*- $[\text{Co}(\text{py})_2\text{Cl}]\text{Cl}$  and the diamine in 2-methoxyethanol solution.

The *tris-cis*-1,2-cyclohexanediamine chromium(III) chloride was prepared from trichlorotris(pyridine)chromium(III) and the diamine in absolute ethanol. In this preparation even very small amounts of water in the diamine or the absolute ethanol resulted in the formation of a violet product, presumably a diol.

*Separation.* All separations of the geometrical isomers and the enantiomers were done by chromatography using SP-Sephadex C-25 cation exchange resin and a suitable eluant.  $[\text{Co}(\text{cis-chxn})_3]^{3+}$  could be separated into both its geometrical isomers and its enantiomers using 0.19 M disodium (+)-tartrate, *mer-Δ* being eluted first. The geometrical isomers and the enantiomers of  $[\text{Cr}(\text{cis-chxn})_3]^{3+}$  could be separated using 0.15 M disodium hydrogenphosphate and 0.2 M disodium (+)-tartrate successively. With phosphate *fac* was eluted first and with (+)-tartrate *Δ* was eluted first. In addition the geometrical isomers of  $[\text{Co}(\text{cis-chxn})_3]^{3+}$  could be separated using 0.25 M sodium (+)-tartratoantimonate(III) the fractions appeared in the order: 1st fraction *mer* and 2nd fraction *fac* as for  $[\text{Co}(\text{meso-bn})_3]^{3+}$  and  $[\text{Co}(\text{meso-ptn})_3]^{3+}$ .<sup>5,6</sup>

*NMR Spectra.* The  $^1\text{H}$  NMR spectrum of *cis*-1,2-cyclohexanediamine has two rather broad peaks at  $\delta$  1.45 and 2.80. The *trans*-1,2-cyclohexanediamine has three multiplets around  $\delta$  1.20, 1.70 and 2.35. The peaks at 2.80 and 2.35, due to the methine protons, do not overlap each other; thus it is possible to measure the relative amounts of *cis* and *trans*-chxn in a mixture with accuracy. The  $^1\text{H}$  NMR spectra of the two geometrical isomers of Co(III) consist of many overlapping lines and are similar, so an identification on this ground is not possible. On the other hand the proton decoupled 15.03 MHz  $^{13}\text{C}$  NMR spectra (Fig. 2) distinguish clearly between the two isomers. As the *facial* isomer has three equivalent chelate rings each with six magnetically nonequivalent carbon atoms one would expect to find six lines as indeed are observed for one of the isomers. The assignment is obtained from the gated  $^1\text{H}$ -coupled  $^{13}\text{C}$  spectrum which shows two doublets for the lines at 56 ppm and 58 ppm and four triplets for the remaining C atoms.

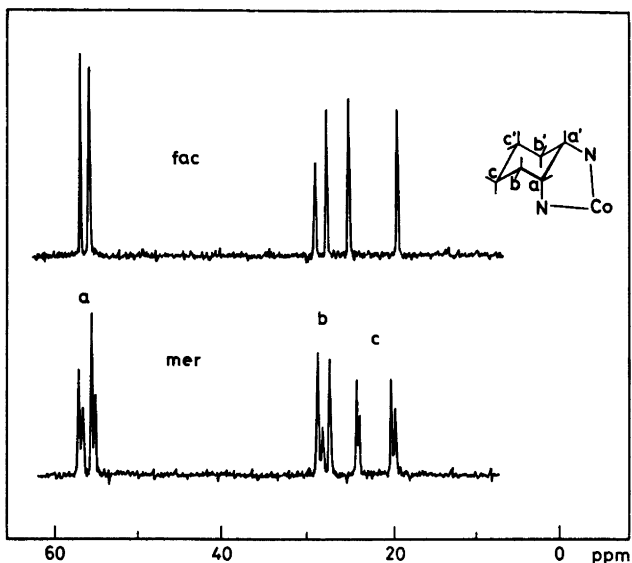


Fig. 2. The 15.03 MHz  $^{13}\text{C}$  NMR spectra of *fac*- and *mer*- $\Delta$ -[Co(*cis*-chxn) $_3$ ] $^{3+}$  in  $\text{D}_2\text{O}$ .

The other isomer exhibits a complicated spectrum with at least 11 lines. Theoretically one would expect 18 lines for the *mer*-isomer. The  $^{13}\text{C}$  NMR spectrum of the free *cis*-1,2-cyclohexanediamine at 30 °C consists of three sharp lines, whereas the spectrum at -50 °C shows six broad lines, indicating that the ring inversion in the cyclohexanering, at 30 °C, is rapid compared with the  $^{13}\text{C}$  frequency. The splitting of the a, b and c carbon signals in the *fac* isomer of [Co(*cis*-chxn) $_3$ ] $^{3+}$  is caused by the interaction of one cyclohexane ring with the other two chelate rings as this interaction is asymmetric in any point of the inversion. Hence the ring inversion in the complexes too are rapid at room temperature and it is impossible to isolate the *tel*- and *ob*- conformers (eight *mer*- and four *fac*-enantiomeric pairs).

**ESR Spectra.** The ESR spectra of the two geometrical isomers of Cr(III) in frozen solution are shown in Fig. 3. Because of the great similarity the assignment is difficult to achieve. The spectrum of isomer *a* has larger line widths and the  $-\frac{3}{2} \rightarrow \frac{3}{2}$  (*z*) transition at 1100 G has gained intensity and moved slightly upfield relative to the spectrum of complex *b*. This suggests that *a* has a larger *E* value than *b* and most probably is the *mer*-isomer.

**The salts.** The identification of the isomers is supported by the fact that the *fac* isomers form the least soluble salts.

It is remarkable that the Cr(III) and Co(III) complexes do not form isomorphous salts, thus co-crystallization could not be detected by ESR measurements. One possible explanation of this fact could be that the Cr(III) and Co(III) complexes have different conformations (at least in the solid state).

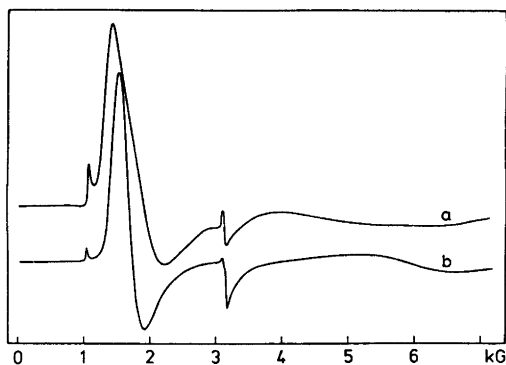


Fig. 3. The ESR spectra of the *mer* (a) and *fac* (b) isomers of  $\Delta$ -[Cr(*cis*-chxn) $_3$ ] $^{3+}$  in frozen solution (DMF,  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$  glass 1:1:2 at -150 °C).

Table 1.

Isomer	Abs		CD		
	$\nu_{\max}$ ( $\epsilon$ )	$\nu_{\max}^a$ ( $\epsilon$ ) <sup>b</sup>	$\nu_{\text{ext}}$ ( $\epsilon_1 - \epsilon_d$ )	$\nu_{\text{ext}}^a$ ( $\epsilon_1 - \epsilon_d$ )	$\nu_{\text{ext}}$ ( $\epsilon_1 - \epsilon_d$ )
$\Delta$ - <i>mer</i> -[Co( <i>cis</i> -chxn) <sub>3</sub> ] <sup>3+</sup>	20.79 (106.6)	28.74 (102.1)	20.02 (-2.89)	27.21 (-0.159)	35.97 +0.63
$\Delta$ - <i>fac</i> -[Co( <i>cis</i> -chxn) <sub>3</sub> ] <sup>3+</sup>	20.88 (99.6)	28.99 (92.8)	20.04 (-2.45)	27.66 (-0.211)	35.71 +0.39
$\Delta$ - <i>mer</i> -[Cr( <i>cis</i> -chxn) <sub>3</sub> ] <sup>3+</sup>	21.28 (93.9)	27.89 (79.0)	21.79 (-2.78)	28.01 (+0.21)	
$\Delta$ - <i>fac</i> -[Cr( <i>cis</i> -chxn) <sub>3</sub> ] <sup>3+</sup>	21.19 (89.4)	27.78 (74.6)	21.65 (-2.38)	27.93 (+0.15)	30.58 (-0.014)

<sup>a</sup>  $\nu_{\max}$  and  $\nu_{\text{ext}}$  in units of 1000 cm<sup>-1</sup>. <sup>b</sup>  $\epsilon$  in units of l mol<sup>-1</sup> cm<sup>-1</sup>.

**Absorption and circular dichroism spectra.** The spectral data are listed in Table 1 and Figs. 4 and 5. The absorption spectra of the *mer* isomers are a little more intense than the *fac* isomers for both Cr(III) and Co(III). And the positions of the maxima are red-shifted for both isomers relative to the tris-*trans*-1,2-cyclohexanediamine complexes,<sup>9</sup> indicating greater steric strain in the former.<sup>10</sup> The CD spectra of the two geometric isomers,

*mer* and *fac*, are similar in shape, but the band intensities of the former are slightly higher than those of the latter, as for the corresponding *meso*-2,4-pentanediamine<sup>5</sup> and *cis*-1,2-cyclopentanediamine complexes,<sup>4</sup> but in contrast to the *meso*-2,3-butanediamine complex.<sup>5</sup> It is interesting that the 2nd band in the CD spectrum of *mer*-[Co(*cis*-chxn)<sub>3</sub>]<sup>3+</sup> is split in two components; it suggests a larger distortion than in the *fac* isomer. The enantiomers with

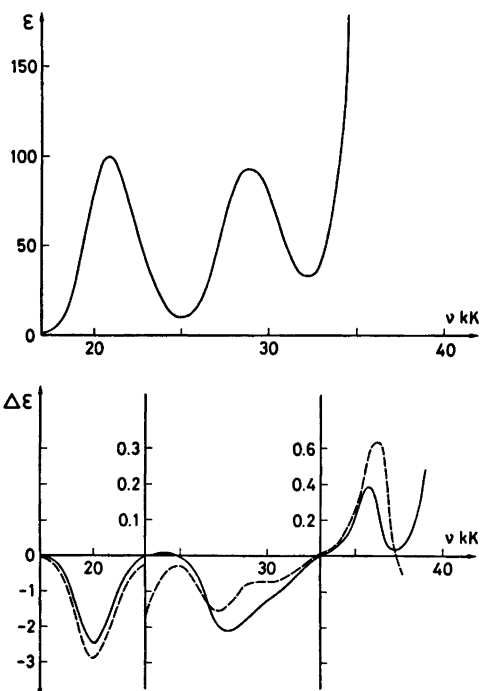


Fig. 4. a. Absorption spectrum of *fac*- $\Delta$ -[Co(*cis*-chxn)<sub>3</sub>]<sup>3+</sup>. b. CD spectra of the *fac*- (—) and *mer*- (---) isomers of  $\Delta$ -[Co(*cis*-chxn)<sub>3</sub>]<sup>3+</sup>.

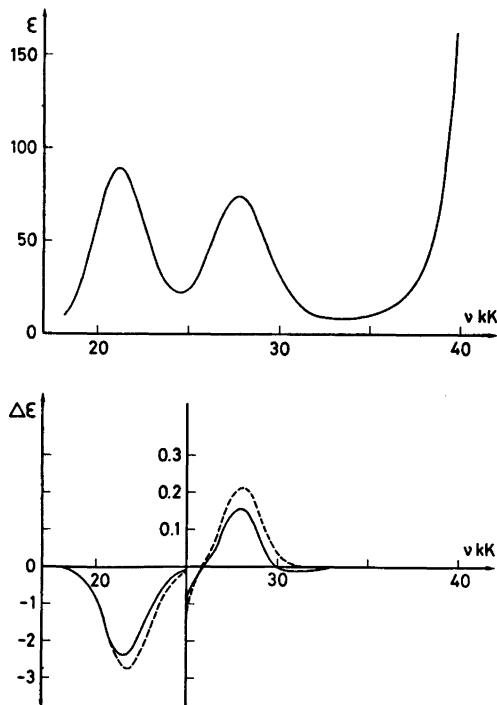


Fig. 5. a. Absorption spectrum of *fac*- $\Delta$ -[Cr(*cis*-chxn)<sub>3</sub>]<sup>3+</sup>. b. CD spectra of the *fac*- (—) and *mer*- (---) isomers of  $\Delta$ -[Cr(*cis*-chxn)<sub>3</sub>]<sup>3+</sup>.

positive main deflections in the first ligand band we assign as  $\Delta$ .<sup>9,11,12</sup>

*Formation ratio.* If the relative abundances of the geometric isomers were governed by statistical consideration alone, the ratio of the *mer* isomer to the *fac* isomer should be 3:1; but Dreiding models indicate a little more steric interaction in the *mer*- than in the *fac*-isomer, Fig 1. Kojima *et al.* found the *mer/fac* ratio 1.4 for  $[\text{Co}(\text{mbn})_3]^{3+}$  and 1.5 for  $[\text{Co}(\text{meso-ptn})_3]^{3+}$ , but these figures may be uncertain as no equilibration of the isomers was performed. In the present work the crude  $[\text{Co}(\text{cis-chxn})_3]\text{Cl}_3$  was separated in the geometrical isomers and the *fac* isomer equilibrated with charcoal at 90 °C according to Harnung.<sup>9</sup>

We found the *mer/fac* ratio to be 1.43. The enthalpy of the transition *fac*→*mer*, after accounting for the statistical entropy contribution is  $\Delta H^\circ = 0.54$  kcal/mol at 90 °C.

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