

The Tris [(±)-*trans*-1,2-cyclohexanediamine]chromium(III) System

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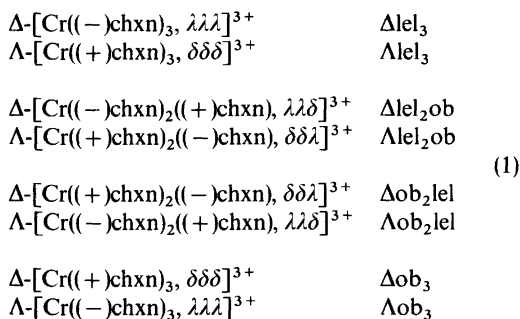
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The eight isomers of $[\text{Cr}(\pm)\text{chxn}]_3^{3+}$ (chxn = *trans*-1,2-cyclohexanediamine) have been isolated. Absorption and circular dichroism spectra are presented of aqueous solutions at *ca.* 300 K in the visible and UV spectral region, and of ethanol/methanol solutions at *ca.* 110 K in the range 610–680 nm of the spin-forbidden transitions.

1. INTRODUCTION

The purpose of this work is an experimental investigation of the electronic transitions of a series of chromium complexes whose geometries resemble the conformations of the tris(ethylenediamine)-chromium(III) ion.

The stereochemistry of the compounds with the formula tris[(±)-*trans*-1,2-cyclohexanediamine]-chromium(III) chloride, $[\text{Cr}(\pm)\text{chxn}]_3\text{Cl}_3$, has been thoroughly discussed in the work¹ on the analogous cobalt(III) complexes. The number of isomers is determined² by the conformation, δ or λ , of each of the five-membered chelate rings and by the configuration, Δ or Λ , around the central metal ion. This gives rise to four racemic pairs of complexes:



Here the symbols *lel* and *ob* (*parallel* and *oblique*) refer to the direction of the bond between the carbon atoms of the chelate ring relative to the threefold axis defined by the three edges of the octahedron which are spanned by the ligands. Thus, the complexes may be classified as lel_3 , lel_2ob , ob_2lel , and ob_3 , each class comprising a Δ and a Λ isomer.

The eight isomers, eqn. (1), can be separated and isolated, as is also the case for the similar complexes of cobalt(III),¹ rhodium(III),³ and iridium(III).⁴ For the analogous tris(ethylenediamine)metal(III) complexes all the isomers of a given configuration are in equilibrium in solution. Accordingly, it is of interest to observe the absorption spectra (ABS) and the circular dichroism spectra (CD) of each of the isomers, and the experimental results are recorded in the present paper.

2. EXPERIMENTAL

Preparation and separation of the isomers. $[\text{Cr}(\text{chxn})_3]\text{Cl}_3$ was prepared according to E. Pedersen⁵ by use of optically active³ or racemic chxn. Ion-exchange separations¹ were carried out at 5 °C in darkness on columns packed with Sephadex Cation Exchanger SP-C25.

Inspection of eqn. (1) shows that in a preparation of $[\text{Cr}((-)\text{chxn})_3]\text{Cl}_3$ only the isomers Δlel_3 and Λob_3 can be obtained. They were formed in the ratio $\Delta\text{lel}_3 - \Lambda\text{ob}_3 = 99:1$. The more abundant isomer was partially removed by repeated precipitation (four times) from a mixture of ethanol–water = 6:1 at –17 °C till the ratio $\Delta\text{lel}_3 - \Lambda\text{ob}_3 = 2:1$ was obtained. The isomers were then separated on a column using 0.1 M trisodium phosphate as eluent. From 39 g of crude $[\text{Cr}((-)\text{chxn})_3]\text{Cl}_3$ we obtained after recryst-

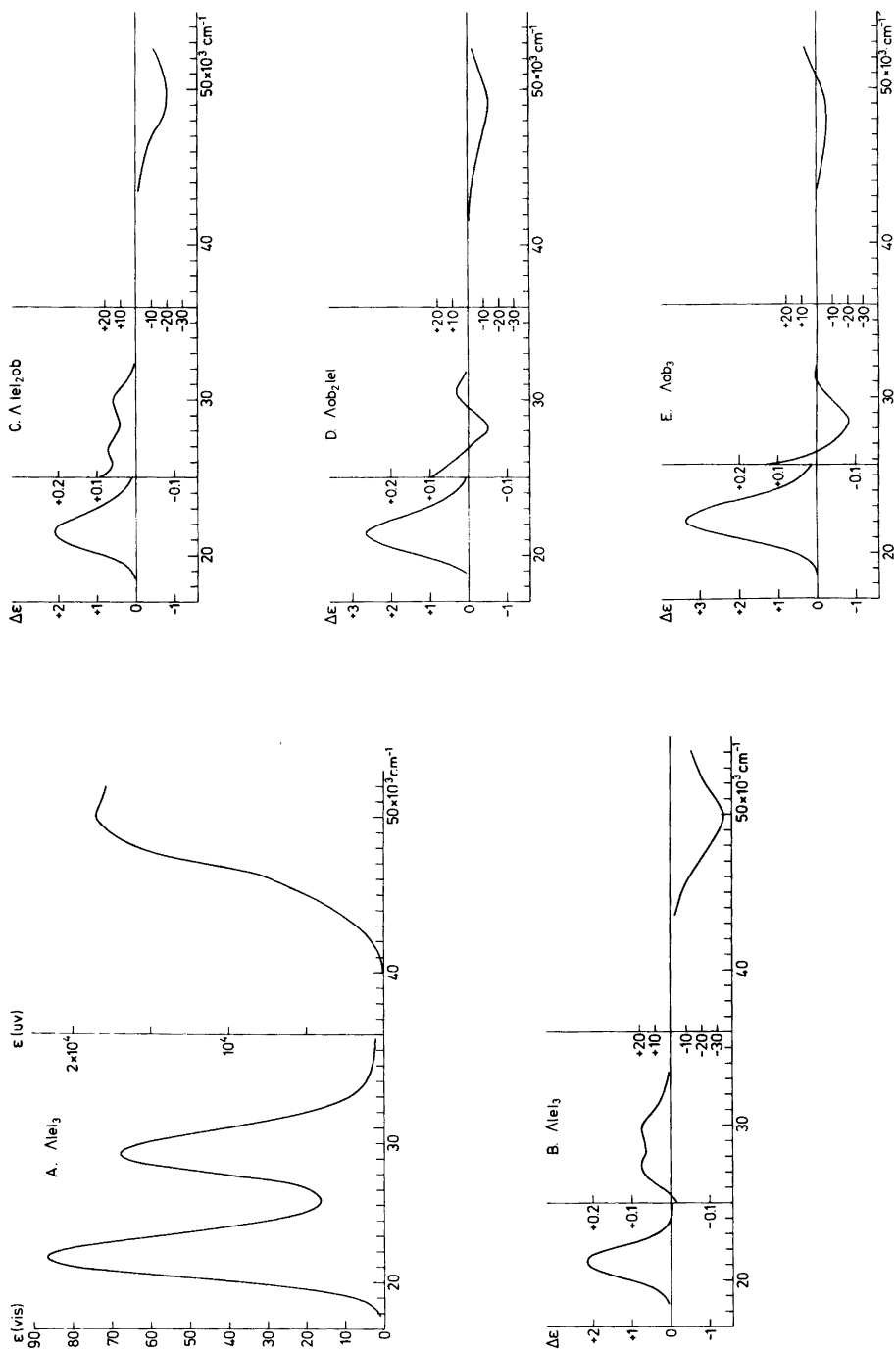


Fig. 1. Absorption and circular dichroism spectra of the spin-allowed transitions of aqueous solutions of the Λ -[Cr(chxn)₃]Cl₃ series at ca. 300 K. The concentrations in the visible spectral region were: A, ABS. and B, CD of Λ -[Cr((+)-chxn)₃, $\delta\delta\delta$]Cl₃ ($0.97 \times 10^{-2} \text{ M}$); C, CD of Λ -[Cr((+)-chxn)₂-] ($1.17 \times 10^{-2} \text{ M}$); D, CD of Λ -[Cr((-)-chxn)₃, $\lambda\lambda\lambda$]Cl₃ ($1.17 \times 10^{-2} \text{ M}$); E, CD of Λ -[Cr((-)-chxn)₃, $\lambda\lambda\lambda$]Cl₃ ($0.95 \times 10^{-2} \text{ M}$). For the UV spectra the solutions were diluted 20-fold for CD and 200-fold for ABS.

Table 1. Spectral data of Λ -[Cr(chxn)₃]Cl₃ at ca. 300 K. The measurements were carried out on Δ lel₃, Δ lel₂ob, Δ lelob₂, and Δ ob₃ in concentrations as stated in the legend to Fig. 1. The molar absorptivity, ϵ , is given for the maximum of the ABS-spectra and $\Delta\epsilon = \epsilon_1 - \epsilon_2$ is given for the extrema of the CD spectra. Unit for $\bar{\nu}$ is 10^3 cm^{-1} .

Δ lel ₃		Δ lel ₂ ob		Δ lelob ₂		Δ ob ₃	
ABS $\bar{\nu}$	CD ($\Delta\epsilon$)	ABS $\bar{\nu}$	CD ($\Delta\epsilon$)	ABS $\bar{\nu}$	CD ($\Delta\epsilon$)	ABS $\bar{\nu}$	CD ($\Delta\epsilon$)
21.69 (87)	21.22(+2.17) 24.5 (-0.03)	21.72 (83)	21.58(+2.10) 26.3 (+0.06)	21.74 (82)	21.83(+2.69)	21.83 (80)	22.00(+3.40)
28.37 (68)	27.3 (+0.08) 28.3 (+0.06) 29.8 (+0.08)	28.37 (68)	26.8 (+0.07) 28.3 (+0.04) 29.9 (+0.05)	28.37 (68)	28.2 (-0.05) 30.5 (+0.03)	28.37 (65)	28.3 (-0.08) 31.5 (+0.01)
50.3(1.85 × 10 ⁴)	49.5 (-34)	50.3(1.95 × 10 ⁴)	49.5 (-20)	50.3(1.91 × 10 ⁴)	49.3 (-14)	50.3(1.85 × 10 ⁴)	48.5 (-7)

tallization from water 30 g of Δ lel₃ and 0.30 g of Δ ob₃.

When [Cr((±)chxn)₃]Cl₃ was prepared from racemic chxn, three racemic pairs of isomers were formed in the ratio lel₃-lel₂ob-ob₂lel=20:4:1, and the pair of ob₃-isomers was not detected. Around 40% of the lel₃-pair was precipitated from a mixture of ethanol-water=1:1 at -17 °C. Then the racemic pairs were separated on a column using 0.1 M trisodium phosphate as eluent, and finally each pair was resolved into optically active components by use of 0.2 M disodium tartrate as eluent. All column separations^{6,2} were quite analogous to those previously described.¹ From 26 g of crude [Cr(±)chxn]₃Cl₃ the yields of recrystallized isomers were: 3 g of each of Δ lel₂ob and Δ lel₂ob, and 0.25 g of each of Δ ob₂lel and Δ ob₂lel.

Identification of the isomers. The absolute configuration of the Δ -[Cr((-)chxn)₃]³⁺ ion has been determined as Δ lel₃ through the X-ray powder spectra⁷ of the active racemate of this compound and Λ -[Co((+)chxn)₃]³⁺ whose absolute configuration⁸ was known. An analogous investigation of the solubility and the X-ray powder spectrum of the active racemate of the chloride of Δ -[Cr((-)chxn)₂((+)chxn)]³⁺ and Λ -[Co((+)chxn)₂((-)chxn)]³⁺, whose absolute configuration⁹ is known, reveals

that the chromium compound is Δ lel₂ob. The absolute configuration of Λ -[Cr((-)chxn)₃]³⁺ follows from the method of preparation and the identification of the Δ -[Cr((-)chxn)₃]³⁺ isomer. Then the identification of the ob₂lel isomers follows from the method of preparation and the CD spectra.

Absorption and circular dichroism spectra. The room temperature spectra were measured on aqueous solutions using a Cary 14 Spectrophotometer and a Jouan Dichrographe 2B. The data are recorded in Table 1 and the spectra are shown in Fig. 1. Molar absorptivities were determined through analyses of the chromium concentrations by means of a Perkin Elmer Atomic Absorption Spectrophotometer 403.

The low temperature glass spectra of the spin-forbidden transitions between 610 and 680 nm, Fig. 2, were measured at ca. 110 K on alcoholic solution ethanol-methanol=5:1. In order to obtain suitable concentrations, the compounds lel₃ acetate, ob₂lel trifluoroacetate, and ob₃ trifluoroacetate were made by metatheses. The solutions were placed in a cryostat cell whose windows were assembled using indium-washers.¹⁰ The CD spectra were recorded on a Roussel Jouan Dichrographe and it was checked that a blank alcoholic solution did not

Table 2. Positions (10^3 cm^{-1}) of the peaks (p) and shoulders (sh) of the ABS and CD around $22 \times 10^3 \text{ cm}^{-1}$ of the Λ [Cr(chxn)₃]³⁺ series ($\sim 10^{-2}$ M in ethanol-methanol=5:1) at ca. 100 K.

Δ lel ₃		Δ lel ₂ ob		Δ lelob ₂		Δ ob ₃	
ABS	CD	ABS	CD	ABS	CD	ABS	CD
21.91 (sh)	21.44 (p)	21.79 (sh)	21.6 (sh)	21.79 (sh)	21.93 (p)	21.74 (sh)	22.0 (sh)
22.22 (p)	22.0 (sh)	22.25 (p)	21.83 (p)	22.25 (p)	22.4 (sh)	22.27 (p)	22.42 (p)
			22.4 (sh)				22.7 (sh)

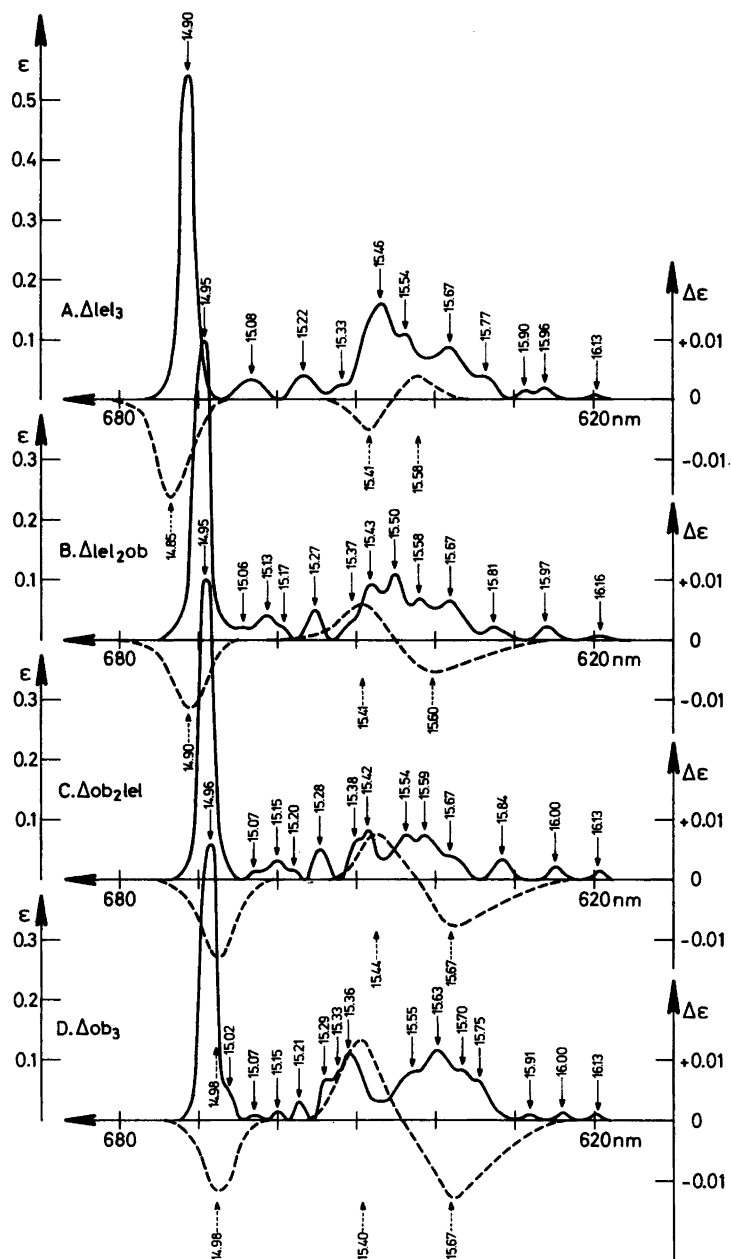


Fig. 2. Absorption spectra (—) and circular dichroism spectra (---) of the spin-forbidden transitions of alcoholic solutions (ethanol:methanol=5:1) of the Δ -[Cr(chxn) $_3$] $^{3+}$ series at ca. 110 K. The spectra are drawn in a wavelength scale, whereas the positions of the peaks are given in units of 10^3 cm^{-1} . The absolute values of ϵ and $\Delta\epsilon$ have not been determined. A, Δ [Cr((-)chxn) $_3$, $\lambda\lambda\lambda$](CH $_3$ COO) $_3$ (5×10^{-2} M); B, Δ [Cr((-)chxn) $_2$ ((+)chxn), $\lambda\lambda\delta$]Cl $_3$ (5×10^{-2} M); C, Δ [Cr((+)chxn) $_2$ (-)chxn), $\delta\delta\lambda$](CF $_3$ COO) $_3$ (4×10^{-2} M); D, Δ [Cr((+)chxn) $_3$, $\delta\delta\delta$](CF $_3$ COO) $_3$ (4×10^{-2} M).

show any birefringence.

The temperature dependence of the spectra. By cooling off the solutions to ca. 110 K the ABS and CD around 22 kK ($1 \text{ K} = 1 \text{ cm}^{-1}$) develop a fine-structure near the peaks. Since the solutions contract considerably, we have in Table 2 only given the positions of the peaks and the shoulders. For all the isomers, the ABS around 28 kK shifts ca. 0.16 kK towards higher energies.

The ABS in the region 610–680 nm changes for all the isomers on cooling. Thus, two small peaks on the low-energy side of the peak at 14.9 kK disappear and the more detailed structure shown in Fig. 2 develops. The temperature dependence of the CD of the lel_3 -isomers is different from that of the other ones: At 300 K the CD of Δlel_3 in the region 630–665 nm is slightly negative, having a minimum at 15.6 kK; at 110 K the spectrum is as shown in Fig. 2. The CD of the three other Δ -isomers does not change much upon cooling.

3. DISCUSSION

The optical transitions between 14 kK and 36 kK can be assigned in the same way as in the $[\text{Cr}(\text{en})_3]^{3+}$ ion (en = ethylenediamine).¹¹ For all the $[\text{Cr}(\text{chxn})_3]^{3+}$ isomers, the transitions can be described in terms of the octahedral parentages as follows:

$$\begin{array}{ll} {}^2E \leftarrow {}^4A_2 & \text{at ca. 15 kK} \\ {}^2T_1 \leftarrow {}^4A_2 & \text{at ca. 15.5 kK} \\ {}^2T_2, {}^4T_2 \leftarrow {}^4A_2 & \text{at ca. 22 kK} \\ {}^4T_1 \leftarrow {}^4A_2 & \text{at ca. 28 kK} \end{array} \quad (2)$$

The spin-forbidden transitions in the region 14.7–16.4 kK (680–610 nm) are particularly interesting. Firstly, the great similarity between the ABS of the lel_3 at 110 K and the polarized spectra¹² of $[\text{Cr}(\text{en})_3]^{3+}$ at 20 K is noted. Secondly, with reference to a recent discussion of the satellite lines that have been observed in the vicinity of the ${}^2E \leftarrow {}^4A_2$ transition in a crystal of $2[\text{Cr}(\text{en})_3]\text{Cl}_3 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ at 1.6 K,¹² the uniform shift of this absorption towards higher energies through the series lel_3 to ob_3 should be recognized. Therefore, the low-energy satellite lines can hardly be due to ob conformations of some of the chelate rings as proposed. Finally, the CD of the ${}^2T_1 \leftarrow {}^4A_2$ transition deserves some comments. The spectra of optically active $[\text{Cr}(\text{en})_3]^{3+}$ at room temperature have been published recently.^{13,14} For the Δ -isomer in a solution of ethanediol–water = 2:1 the CD-peaks are¹⁴

$$\begin{array}{ll} 14.94 \text{ kK}, & \Delta\epsilon = -0.016 \\ 15.25 \text{ kK}, & \Delta\epsilon = +0.007 \\ 15.55 \text{ kK}, & \Delta\epsilon = -0.007 \end{array} \quad (3)$$

By comparison of the spectra in Fig. 2, taking into account the temperature dependence of the lel_3 spectrum, and the data of eqn. (3), one can infer that a minor part of $[\text{Cr}(\text{en})_3]^{3+}$ in solution is the lel_3 conformer.

The trigonal components of the 2T_1 level in $[\text{Cr}(\text{en})_3, lel_3]^{3+}$ have been assigned on the basis of the polarized crystal spectra.¹² Since the Δlel_3 -isomer has the same symmetry, D_3 , we propose that the CD at 15.41 kK is due to the transition ${}^2E({}^2T_1) \leftarrow {}^4A_2$ and that the CD at 15.58 kK is due to ${}^2A_2({}^2T_1) \leftarrow {}^4A_2$. On this basis and the CD of the ob_3 -isomer we assign the CD at 15.40 kK of this isomer as due to the transition ${}^2A_2({}^2T_1) \leftarrow {}^4A_2$ and 15.67 kK as due to ${}^2E({}^2T_1) \leftarrow {}^4A_2$. Apparently, the magnitude of the splitting increases from lel_2ob through ob_2lel to ob_3 .

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