

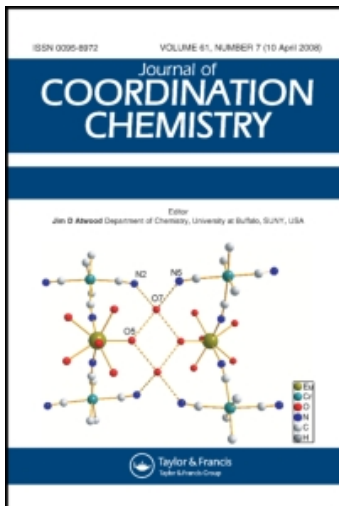
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Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

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To cite this Article Brennan, Bernard J. and Douglas, Bodie E.(1972) 'CHARACTERIZATION OF *CIS*- AND *TRANS*-DINITROBIS-(*l*-CYCLOHEXANEDIAMINE)-COBALT(III) CHLORIDE¹', Journal of Coordination Chemistry, 1: 4, 297 – 300

To link to this Article: DOI: 10.1080/00958977208072934

URL: <http://dx.doi.org/10.1080/00958977208072934>

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CHARACTERIZATION OF *CIS*- AND *TRANS*-DINITROBIS-(*L*-CYCLOHEXANEDIAMINE)-COBALT(III) CHLORIDE¹

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(Received April 14; in final form November 16, 1971)

Two geometrical isomers of $[\text{Co}(l\text{-chxn})_2(\text{NO}_2)_2]\text{Cl}$ have been isolated. The *trans*-isomer is eluted first from a cellulose ion exchange column as a single isomer. The *cis*-isomer corresponds to the complex previously reported as the *trans*-isomer. The *cis*-isomer with the same CD sign pattern as for the *trans*-isomer is stereoselectively favored, but a small amount of the second *cis*-isomer separates using Cellex CM ion exchange cellulose. The CD spectra of the *cis*- and *trans*- isomers are similar to those of the corresponding isomers of the *l*-pn complex.

INTRODUCTION

The *cis*²- and *trans*³-isomers of $[\text{Co}(l\text{-pn})_2(\text{NO}_2)_2]^+$ ion⁴ have been characterized and their circular dichroism (CD) spectra reported. The possibility has been suggested⁵ that Wentworth and Piper³ had *cis*- rather than the reported *trans*- $[\text{Co}(l\text{-pn})_2(\text{NO}_2)_2]^+$ ion, but their results are now verified. Treptow⁶ reported a series of complex ions of the type $\text{trans}-[\text{Co}(l\text{-chxn})_2\text{X}_2]^{n+}$, including $\text{trans}-[\text{Co}(l\text{-chxn})_2(\text{NO}_2)_2]^+$, giving CD, ORD, and adsorption data. He accounted for the unusually intense CD peaks in the visible region for the presumed *trans*-dinitro complex as the result of mixing of charge transfer character with the *d-d* transitions. Both *cis*- and *trans*-isomers of $[\text{Co}(l\text{-chxn})_2(\text{NO}_2)_2]^+$ are now reported and Treptow's complex corresponds to the *cis*-isomer.

EXPERIMENTAL SECTION

Preparation of l-cyclohexanediamine d-tartrate

1,2-Diaminocyclohexane, the proportions of the *cis*- and *trans*-isomers being unknown, was purchased from Aldrich Chemical Company (the product used to be designated as *trans*). The resolution^{5,7} of the *trans*-isomer was accomplished by precipitation of the amine (as purchased) as the diastereomer, *l*-chxn *d*-tartrate, using a 1:1 mole ratio of amine to *d*-tartaric acid. The less soluble diastereoisomer was recrystallized (2 or 3 times) from hot water to a constant optical rotation, $[\alpha]_{589} +12.0^\circ$ [lit. (+11°)⁶, (+12°)⁵].

Preparation of *trans*-Dichlorobis(*l*-cyclohexanediamine)-cobalt(III) Chloride Monohydrate. This complex was prepared by a modification of earlier methods.^{6,8} An aqueous solution of *l*-chxn was prepared by adding $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (54.5 g, 0.173 mole) to a stirred suspension of *l*-chxn *d*-tartrate (45.3 g, 0.173 mole) in warm water (400 ml, 65°). The mixture was heated with stirring for 90 min, then cooled in an ice bath for 2 hr, and filtered to remove barium tartrate. To the filtrate was added $[\text{Co}(\text{NH}_3)_4\text{CO}_3]\text{NO}_3 \cdot 1/2\text{H}_2\text{O}$ ⁹ (25.8 g, 0.1 mole), followed by stirring for 15 min and then heating on a steam bath for 4½ hr. After the solution had cooled to 10° in an ice bath, it was filtered and concentrated HCl (100 ml) was slowly and cautiously added with vigorous stirring. This solution was then evaporated almost to dryness on a steam bath, cooled in ice to 10°, and then filtered. The residue was then triturated with acetone until the filtrate was nearly colorless. Twenty-five grams of crude product, which contained a mixture of *cis*- and *trans*- $[\text{Co}(l\text{-chxn})_2\text{Cl}_2]\text{Cl} \cdot n\text{H}_2\text{O}$, was obtained.

The product was converted to *trans*- $[\text{Co}(l\text{-chxn})_2\text{Cl}_2]\text{Cl} \cdot n\text{H}_2\text{O}$ by refluxing the crude material (8 g) in 200 ml of absolute methanol for 90 min. The hot methanolic solution was then filtered and, upon cooling in ice, green *trans*- $[\text{Co}(l\text{-chxn})_2\text{Cl}_2]\text{Cl} \cdot 1/2\text{H}_2\text{O}$ precipitated. The optically pure product as the hemihydrate gave $\Delta\epsilon_{610} +0.96$ (lit.⁶ for $[\text{Co}(l\text{-chxn})_2\text{Cl}_2]\text{ClO}_4$, $\Delta\epsilon_{610} +0.93$).

Cis- and *Trans*-Dinitrobis(*l*-cyclohexanediamine) cobalt(III) Chloride Hemihydrate. The complex

was prepared by a procedure based on the preparation¹⁰ of *cis*-[Co(en)₂(NO₂)₂]⁺ ion. The complex *trans*-[Co(*l*-chxn)₂Cl₂]Cl (3.0 g, 0.0076 mole) was dissolved in water (55 ml) by warming the suspension to 40–45° with stirring. A solution of KNO₂ (2.3 g, 0.027 mole) in water (20 ml) was added with stirring and within a few min the solution turned orange and precipitation commenced. The mixture was heated and stirred for 2 hr while the volume decreased to 60 ml. The solution was cooled in ice, filtered, and the precipitate washed successively with a few ml of H₂O, acetone, ether and air dried. Yield: 0.9 g. The first fraction was relatively insoluble in water (*ca.* 0.7 g/l) and contained the *cis* isomer. Recrystallization was effected by dissolution in a minimum amount of hot water, cooling overnight in a refrigerator (5°), filtering and washing as before. The complex was recrystallized three times.

The filtrate obtained from the first filtration (*ca.* 60 ml) was reduced further in a stream of compressed air and seven fractions were obtained. Initial fractions contained the *cis*-isomer and the

later fractions the *trans*-isomer. Similar fractions were combined and recrystallized from water.

Cellex CM and Cellex P ion exchange cellulose columns (2.2 × 40 cm) were used for checking the purity of the isomers. Samples were eluted with 0.01 M NaCl. The optically pure *cis*-isomer was recovered from the combination of later fractions with similar CD spectra which were evaporated to dryness. The NaCl was leached from the residue with a few drops of water and finally the residue was recrystallized from the minimum amount of hot water ($\Delta\epsilon_{466} = -1.77$).

Anal. Calcd. for CoC₁₂H₂₈N₆O₄Cl·1/2H₂O: C, 34.00; H, 6.85; N, 19.81. Found *cis*-isomer: C, 34.37; H, 6.78, N, 20.06; *trans*-isomer: C, 33.67; H, 6.87; N, 20.20.

Cis- and *Trans*-Dinitrobis(*l*-propylenediamine)-cobalt(III) Salts. The *cis*-complex was prepared from *trans*-[Co(*l*-pn)₂Cl₂]Cl¹¹ and KNO₂ as for the *l*-chxn complex above. The active *cis*-complex was obtained by recrystallization without using a resolving agent. The *cis*-[Co(*l*-pn)₂(NO₂)₂]Cl was refluxed for 26–30 hr as described by O'Brien,

TABLE I
Circular dichroism and absorption spectral data for some
Cis- and *Trans*-Dinitrobis(diamine)cobalt(III) complexes

Complex ¹³	Absorption		CD	
	cm ⁻¹	ϵ	cm ⁻¹	$\Delta\epsilon$
Δ - <i>cis</i> -[Co(<i>l</i> -chxn) ₂ (NO ₂) ₂]Cl·1/2H ₂ O	22,800	208	21,500	-1.77
	30,900	4,450	24,100	+0.99
<i>cis</i> -[Co(<i>l</i> -chxn)(NO ₂) ₂]NO ₃ (Reported ⁵ as the <i>trans</i> isomer)	22,800	193	21,500	-1.61
	31,100	4,100	24,400	+0.98
Δ - <i>cis</i> -[Co(<i>l</i> -pn) ₂ (NO ₂) ₂]I	22,900	226	21,750	-1.32
	31,450	3,890	24,400	+0.67
Λ - <i>cis</i> -[Co(en) ₂ (NO ₂) ₂]Cl ¹⁴	22,700	224	21,700	+1.4
	30,800	3,800	25,000	-0.65
<i>trans</i> -[Co(<i>l</i> -chxn) ₂ (NO ₂) ₂]Cl·1/2H ₂ O	23,000	183	21,600	-0.93
	29,200	3,240	24,400	+0.49
<i>trans</i> -[Co(<i>l</i> -pn) ₂ (NO ₂) ₂]ClO ₄ Ref. 3	23,100	165	21,700	-0.62
			24,500	+0.44
This work	23,100	165	21,700	-0.83
	29,360	3,310	24,500	+0.46

McReynolds, and Bailar.¹² The resulting solution was poured through a Cellex P (Na form) ion exchange column (0.8 × 40 cm) and eluted with 0.05 M NaBr. Conversion to the *trans*-isomer was incomplete since the two isomers separated on the column. The *trans*-isomer eluted first and was recrystallized for spectral measurements. The red-orange crystals did not lose weight after drying at 105° C overnight.

Spectral Measurements

Visible absorption spectra were recorded at room temperature on a Cary Model 14 spectrophotometer using a tungsten lamp. Circular dichroism spectra ($\Delta\epsilon$ in $M^{-1}cm^{-1}$) were recorded on a Roussel-Jouan Dichrographe using a Sylvania Sun Gun light source. Measurements were made at room temperature on aqueous solutions in a 2 cm quartz cell. The concentration of the aqueous solutions was approximately 10^{-3} M for adsorption and CD spectra.

RESULTS

The less soluble isomer of $[Co(l-chxn)_2(NO_2)_2]Cl$ (from early fractions) was passed through a Cellex CM column. The first fraction eluted gave a positive CD peak in the region of the first absorption band. Its absorption spectrum was identical to those of later fractions. The amount of this isomer was too small for isolation. Fractions after the first gave two CD peaks of opposite sign in the visible region (*cis*-isomer in Figure 1 and Table I). The more soluble isomer (*trans*) gave identical CD ($\Delta\epsilon_{462} = -0.92$) and absorption spectra for all fractions using the same Cellex CM exchange column as above.

A mixture of 0.1 g of the *cis*- and *trans*- $[Co(l-chxn)_2(NO_2)_2]^+$ isomers in ca. 150 ml of water did not separate into distinct bands on a Cellex CM column, but 2 narrow, well separated bands were obtained using Cellex P (25 g) eluted with 0.01 M NaCl. The more soluble (*trans*) isomer is eluted first.

The absorption and CD spectra of the *cis*- $[Co(l-pn)_2(NO_2)_2]^+$ ion reported here (Table I) agreed with those reported² along with the determination of the absolute configuration for $\Delta-(+)_589$ -*cis*- $[Co(l-pn)_2(NO_2)_2]Cl$.

The two geometric isomers of $[Co(l-chxn)_2(NO_2)_2]Cl$ differ in their separation into distinct bands on Cellex P, in solubility, and in absorption and CD spectra. The more soluble

isomer is eluted first, as expected for a *trans*-isomer. It gave no indication of the presence of more than one optical isomer on Cellex CM. The lower intensity CD peaks, in comparison to the other isomer (Figure 1), are expected for the *trans* isomer which has no net chirality with respect to the two chelate rings. Its CD intensities are very similar to those³ of *trans*- $[Co(l-pn)_2(NO_2)_2]^+$ (Table I). This new isomer can be confidently assigned as *trans*- $[Co(l-chxn)_2(NO_2)_2]Cl$.

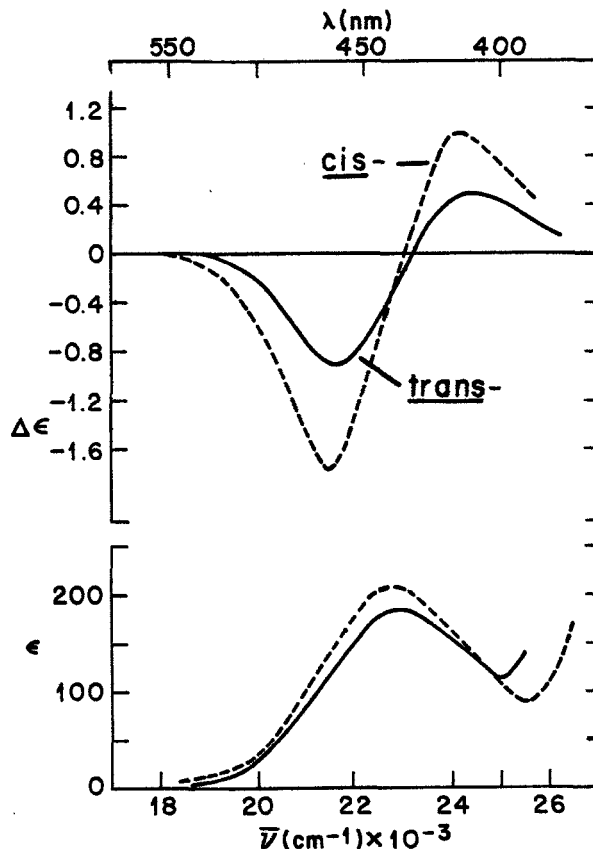


FIGURE 1 Circular dichroism and absorption spectra of *cis*- and *trans*- $[Co(l-chxn)_2(NO_2)_2]Cl \cdot 0.5H_2O$.

DISCUSSION

Buckingham, Marzilli, and Sargeson⁵ questioned the identity of the reported⁶ *trans*- $[Co(l-chxn)_2(NO_2)_2]^+$ because of the absorption spectrum. They also believed that the reported incomplete second absorption band of *trans*- $[Co(l-pn)_2(NO_2)_2]^+$ indicated that it was really the

cis-isomer. The maximum of the second absorption band (Table I) is actually at $29,360\text{ cm}^{-1}$, not in the region expected for a *cis*-isomer. The absorption and CD spectra reported here are in good agreement with those reported by Wentworth and Piper. These results and the ion exchange chromatographic separations confirm the identity of this as *trans*-[Co(*l*-pn)₂(NO₂)₂]⁺.

The less soluble isomer of the *l*-chxn complex when passed through Cellex CM gave a small fraction with a single positive CD peak in the $22,000\text{ cm}^{-1}$ region. This is interpreted as the optically impure second isomer of *cis*-[Co(*l*-chxn)₂(NO₂)₂]⁺. The *cis*-isomer which formed stereo-selectively in larger amount gives a CD spectrum (Figure 1 and Table I) very similar to that² of $\Delta-(+)$ ₅₈₉-*cis*-[Co(*l*-pn)₂(NO₂)₂]⁺.¹³ The close correspondence between the CD spectrum for this pn complex and that for the *cis*-[Co(*l*-chxn)₂(NO₂)₂]⁺ reported here establishes the Δ configuration for the latter complex also. This assignment does not involve the usual spectral uncertainties with respect to identification of transitions and possible inversions in comparison to other *cis*-diacido complexes.

The isomer reported by Treptow⁶ as *trans*-[Co(*l*-chxn)₂(NO₂)₂]⁺ must be the *cis*-isomer. The slight variation in spectral data from those reported here can be accounted for by the fact that he had a nitrate salt containing some of the opposite optical isomer. One optical isomer is formed stereoselectively, but the small amount of the other optical isomer is not removed effectively by crystallization. It is removed effectively by chromatographic separation. The spectral intensities are normal for a *cis*-isomer.

The *trans*-[Co(*l*-pn)₂(NO₂)₂]⁺ ion reported by Wentworth and Piper³ is confirmed and the absorption and CD spectra correspond closely to those of the newly prepared *trans*-[Co(*l*-chxn)₂(NO₂)₂]⁺. The *cis* and *trans*-isomers of both *l*-pn and *l*-chxn complexes give remarkably similar CD spectra in the visible region, differing primarily in intensities.

ACKNOWLEDGMENT

The authors are grateful to Mr. John M. Preston for preparing the *l*-pn complexes in order to verify the identity of *trans*-[Co(*l*-pn)₂(NO₂)₂]⁺ and serve as reference compounds for the *l*-chxn complexes.

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