

Stereochemical Studies of Metal Chelates. VIII.<sup>1</sup> Absolute Configuration and Circular Dichroism of Cobalt(III) Complexes with 4,7-Diaza-1,10-diaminodecane (3,2,3-tet) Derivatives

M. Saburi, C. Hattori, and S. Yoshikawa

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Optically active tetradentate ligands, *N,N'*-bis( $\gamma$ -aminopropyl)-*R*-1,2-diaminopropane (= *R*-ap<sub>pn</sub>), *N,N'*-bis( $\gamma$ -aminopropyl)-*R*-1,2-diaminocyclohexane (= *R*-ap<sub>ch</sub>n), and *N,N'*-bis( $\gamma$ -aminopropyl)-(*R*)-2,3-diaminobutane (= (*R*)-ap<sub>bn</sub>; optical purity, 10%) were prepared. The *trans*-dichlorocobalt(III) complexes and oxalato-cobalt(III) complexes with these ligands were prepared and characterized. The (–)<sub>D</sub>-*trans*-Co(3,2,3-tet)Cl<sub>2</sub><sup>+</sup> ion was determined to have the *SS* absolute configuration with respect to the coordinated secondary nitrogen centers, based on the similarity in the circular dichroism (CD) curves of this ion, and the *R*-ap<sub>pn</sub> and *R*-ap<sub>ch</sub>n complexes. The *SS* absolute configuration of the latter complexes was estimated on the basis of the stereospecificity expected for the used asymmetric ligands. The topology of the oxalato complexes with 3,2,3-tet and its derivatives was determined to be the *cis*- $\beta$  structure from the proton magnetic resonance spectrum of Co((*R*)-ap<sub>bn</sub>)ox<sup>+</sup> ion.

## Introduction

The ligand stereospecificity<sup>2</sup> attending to optically active multidentate ligands has often served to elucidate the stereochemistry of the metal complexes coordinated with parent unsubstituted ligands. The usefulness of the stereospecificity has been typically demonstrated in determining the absolute configuration of the resolved enantiomer of the parent complex. For example, the absolute configuration of the optically-active antipode of ethylenediaminetetraacetato-cobaltate(III) ion has been clarified by examining the active propylenediaminetetraacetato complex.<sup>3,4</sup> The absolute configuration of the resolved enantiomorphs of *N*-methylethylenediamine complexes has also been ascertained by the use of optically-active *N*-methylpropylenediamine as the corresponding active ligand.<sup>5,6</sup>

We attempted to determine the absolute configuration of the active enantiomer of cobalt(III) complexes with 4,7-diaza-1,10-diaminodecane (3,2,3-tet) by utilizing optically active derivatives of 3,2,3-tet, in a similar manner as above.

There are three topological isomers for diacidocobalt(III) complexes of 3,2,3-tet, as is shown in Figure 1. Furthermore, three isomers are possible for the *trans* geometry because of the asymmetric character of the coordinated secondary nitrogen atoms, as shown in Figure 2. *R* and *S'* refer to the absolute configuration of asymmetric secondary N centers. Hence, the three isomers are represented as *RR*, *SS*, and *RS* (Figure 2) by the combination of the absolute configuration of two secondary N centers. The *RR* and *SS* forms are enantiomeric to each other, while the *RS* form is intrinsically inactive (meso). For the *RS* form, the central diamine chelate ring has the eclipsed envelope conformation; for the *RR* and *SS* configuration, the central chelate ring adopts the *gauche* conformation. Both of the six-membered chelate rings probably adopt the chair conformation as is shown in Figure 2. The *trans*-Co(3,2,3-tet)Cl<sup>+</sup> complex so far

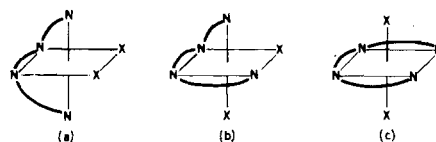


Figure 1. Topological isomers of 3,2,3-tet complex: (a) *cis*- $\alpha$ , (b) *cis*- $\beta$ , and (c) *trans*.

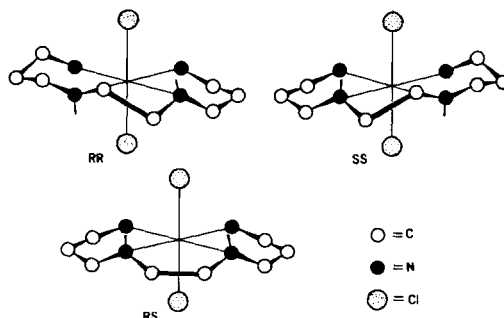


Figure 2. Possible isomers of *trans*-Co(3,2,3-tet)Cl<sub>2</sub><sup>+</sup> ion; *RR*, *SS*, and *RS* forms.

(1) Part VII. M. Saburi, T. Sawai, and S. Yoshikawa, *Bull. Chem. Soc. Japan*, **45**, 1086 (1972).

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(3) F. P. Dwyer and F. L. Garvan, *J. Amer. Chem. Soc.*, **83**, 2610 (1961).

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(5) M. Saburi, Y. Tsujito, and S. Yoshikawa, *Inorg. Nucl. Chem. Letters*, **5**, 203 (1969).

(6) M. Saburi, Y. Tsujito, and S. Yoshikawa, *Inorg. Chem.*, **9**, 1476 (1970).

prepared has been determined to be the racemic form.<sup>8</sup>

Recently, Brubaker and Schaefer obtained the optically active form of *trans*-[Co(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub>,<sup>9,10</sup> and reported its circular dichroism (CD) spectrum.<sup>11</sup> These authors<sup>9,10</sup> assigned the absolute structure of the (-)<sub>D</sub>-*trans*-Co(3,2,3-tet)Cl<sub>2</sub><sup>+</sup> ion to the RR configuration, comparing its CD curve with that of the active *trans*-dichloro complex of triethylenetetramine(trien). The absolute configuration of the trien complex had been established.<sup>12</sup>

We noticed that the conformation of the central ethylenediamine moiety is correlated to the configuration of the secondary N atoms; the RR configuration adopts the δ conformation, and the SS configuration takes the λ conformation, as is indicated in Figure 2. If the conformation of the central diamine linkage of 3,2,3-tet system is fixed in the λ conformation, the *trans* complex gives rise to the SS configuration stereospecifically. On this basis, we prepared 4,7-diaza-5(R)-methyl-1,10-diaminodecane (or N,N'-bis(γ-amino-propyl)-R-1,2-diaminopropane; R-appn), which is a derivative of 3,2,3-tet, with a methyl group on the central ethylenediamine moiety. The structure and the abbreviations of tetramine ligands synthesized in this study are summarized in Table I. The ligand

Table I.

Ligands	Abbreviations
$\begin{array}{c} \text{CH}_3 \\   \\ \text{NH}_2(\text{CH}_2)_2\text{NH}-\text{C}-\text{CH}_2\text{NH}(\text{CH}_2)_2\text{NH}_2 \\   \\ \text{H} \end{array}$	R-appn
$\begin{array}{c} \text{NH}_2(\text{CH}_2)_2\text{NH} \quad \text{NH}(\text{CH}_2)_2\text{NH}_2 \\ \diagdown \quad \diagup \\ \text{Cyclohexane ring} \end{array}$	R-apchn
$\begin{array}{c} \text{CH}_3 \quad \text{H} \\   \quad   \\ \text{NH}_2(\text{CH}_2)_2\text{NH}-\text{C}-\text{C}-\text{NH}(\text{CH}_2)_2\text{NH}_2 \\   \quad   \\ \text{H} \quad \text{CH}_3 \end{array}$	(R)-apbn

R-appn, has the R configuration with respect to the asymmetric carbon atom. The central diamine chelate ring of this ligand should have the λ conformation, so far as the substituted methyl group takes preferentially the equatorial orientation. The predominance of the equatorial orientation has been established for the methyl group(s) in a number of trien derivatives.<sup>1,13,14</sup> Thus, the *trans*-dichlorocobalt(III) complex of R-appn should, stereospecifically, have the SS con-

figuration. The CD curve of this complex was expected to be antimeric to that of the (-)<sub>D</sub>-*trans*-Co(3,2,3-tet)Cl<sub>2</sub><sup>+</sup> ion, if the assignment by Brubaker and Schaefer is correct. It was found, however, that the CD curve of the *trans*-Co(R-appn)Cl<sub>2</sub><sup>+</sup> ion is very similar to that of the (-)<sub>D</sub>-*trans*-Co(3,2,3-tet)Cl<sub>2</sub><sup>+</sup> ion, suggesting that some revisions are required with regard to the structural assignments of 3,2,3-tet complexes given by Brubaker *et al.*

## Experimental Section

**Phthalyl-β-alanine.** This was prepared by fusing a mixture of β-alanine (1 mole) and phthalic anhydride (1 mole) in an oil bath at 160° for 2 hr, according to a usual procedure for preparing phthalic amino acids.<sup>15</sup> The product was recrystallized from methanol and dried in vacuo, m.p. 156.0-157.0°

**Phthalyl-β-alanyl chloride.** In a 500 ml Erlenmeyer flask equipped with a reflux condenser protected with a calcium chloride drying tube, 120 g of phthalyl-β-alanine and 240 ml of thionyl chloride were added. The mixture was heated at 60° for 30 min with occasional stirring. After the reaction mixture had been cooled, the excess thionyl chloride was removed under reduced pressure, and the solidified product was recrystallized from hot toluene. The pure product was filtered off, and washed with toluene and petroleum ether, and dried under vacuum. Yield, 110 g. m.p. 108-109°.

**R(-)<sub>D</sub>-Propylenediamine.** Commercially available *dl*-propylenediamine was resolved by the method of Dwyer *et al.*,<sup>16</sup> and the desired enantiomer was recovered by distillation.

**N,N'-bis(phthalyl-β-alanyl)-R-1,2-diaminopropane.** R(-)<sub>D</sub>-propylenediamine (10.0 g) and sodium carbonate (15.0 g) were dissolved in 150 ml of water, and the solution was cooled in an ice bath to 10°. To this solution, a solution of phthalyl-β-alanyl chloride (62.0 g) in dioxane (150 ml) was added dropwise with vigorous stirring by means of a blender. The temperature of the reaction mixture was maintained below 10° during the addition by external cooling with an ice bath. After the addition had been completed, the white precipitates, thus formed, was filtered off, and washed with water and methanol. The crude product was recrystallized from boiling acetic acid. Yield, 27 g. *Anal.*, Calcd for C<sub>25</sub>H<sub>24</sub>N<sub>4</sub>O<sub>6</sub>: C, 63.01; H, 5.08; N, 11.76%. Found: C, 62.96; H, 5.16; N, 11.77%.

**N,N'-bis(β-alanyl)-R-1,2-diaminopropane hydrochloride.** N,N'-bis(phthalyl-β-alanyl)-R-1,2-diaminopropane (23.8 g, 0.05 mole) and hydrazine hydrate (5.0 g, 0.10 mole) were added to 500 ml of ethanol, and the mixture was heated under reflux for 3 hr; the mixture was then cooled to room temperature, and allowed to stand overnight. The mixture was evaporated un-

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(9) G. R. Brubaker and D. P. Schaefer, *ibid.*, **9**, 2373 (1970).

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(12) D. A. Buckingham, P. A. Marzilli, A. M. Sargeson, S. F. Mason, and P. G. Beddoe, *Chem. Commun.*, 433 (1967).

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(16) F. P. Dwyer, F. L. Garvan, and A. Shulman, *ibid.*, **81**, 290 (1959).

der reduced pressure almost to dryness. To the remaining solid mass, 100 ml of 1 N hydrochloric acid and 50 ml of water were added, and the resultant mixture was warmed on a water bath for 30 min and, then, cooled to room temperature overnight. The insoluble white precipitates were filtered off, and, washed with water. The filtrate and washings were combined and, then, concentrated under reduced pressure to a volume of 50 ml. The solution was stood in a refrigerator overnight. A small amount of white precipitates which appeared were filtered off, and washed with a small volume of water. The filtrate and washings were combined, and concentrated under reduced pressure. The yellow viscous residue, which remained, was used in the following reaction without further purification.

*N,N'*-bis( $\gamma$ -aminopropyl)-*R*-1,2-diaminopropane (4,7-diaza-5(*R*)-methyl-1,10-diaminodecane). To *N,N'*-bis( $\beta$ -alanyl)-*R*-1,2-diaminopropane obtained as above (0.05 mole scale), 250 ml of anhydrous tetrahydrofuran was added. Then, lithium aluminium hydride (11.4 g) was added to the mixture with stirring. After the exothermic effervescence had been completed, the mixture was heated under reflux with stirring for 24 hr, and, then, cooled to room temperature. 21 ml of water diluted with 30 ml of tetrahydrofuran was carefully added dropwise with vigorous stirring. The resultant slurry was filtered off, and washed with tetrahydrofuran (100 ml). The residue was extracted with tetrahydrofuran (150 ml) under reflux for 2 hr, and filtered off, and washed as above. All the filtrates and washings were combined, and tetrahydrofuran was removed by distillation. The remaining oily liquid was distilled under reduced pressure, b.p. 120-122° (2 mm). Yield 1.60 g.

Trans-dichloro(*N,N'*-bis( $\gamma$ -aminopropyl)-*R*-1,2-diaminopropane)cobalt(III) perchlorate, (trans-[Co(*R*-apppn)Cl<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>). To a solution of 2.04 g of CoCl<sub>2</sub>·6C<sub>2</sub>O in 30 ml of water, 1.60 g of *R*-apppn was added. After a few drops of concentrated HCl had been added, the solution was aerated for 8 hr. 10 ml of concentrated HCl was added to the solution, and the resultant solution was concentrated on a water bath, until a small amount of green crystals began to separate. 5 ml of 60% HClO<sub>4</sub> was added to this solution, and the mixture was cooled in an ice bath. The green crystals, which separated, were filtered off, and washed with cold water, methanol and acetone, and air-dried. Yield 3.25 g. The crude product was recrystallized from dilute HCl. *Anal.*, Calcd for [Co(C<sub>9</sub>H<sub>24</sub>N<sub>4</sub>)Cl<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>: C, 25.89; H, 5.80; N, 13.41 percent. Found: C, 26.30; H, 5.88; N, 13.12%.

$\Delta$ - $\beta$ -oxalato(*N,N'*-bis( $\gamma$ -aminopropyl)-*R*-1,2-diaminopropane)cobalt(III) perchlorate ( $\Delta$ - $\beta$ -[Co(*R*-apppn)ox](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O). 0.84 g of trans-[Co(*R*-apppn)Cl<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> and 0.27 g of sodium oxalate were added to 10 ml water, and the resultant suspension was heated on a steam bath. When the mixture turned to a deep red-colored solution, this was cooled in an ice bath. The red crystals, which separated, were collected by filtration, washed with cold water, ethanol and acetone,

and air-dried. Yield, 0.53 g. *Anal.*, Calcd for [Co(C<sub>9</sub>H<sub>24</sub>N<sub>4</sub>)(C<sub>2</sub>O<sub>4</sub>)]ClO<sub>4</sub>·H<sub>2</sub>O: C, 29.17; H, 5.79; N, 12.38%. Found: C, 29.20; H, 5.82; N, 12.48%.

*R*(-)-*D*-1,2-Diaminocyclohexane. Commercially available 1,2-diaminocyclohexane was resolved by the method of Asperger and Liu.<sup>17</sup> The *R*(-) antipode was obtained as its hydrochloride.

*N,N'*-bis(phthalyl- $\beta$ -alanyl)-*R*-1,2-diaminocyclohexane. 14.3 g of *R*-1,2-diaminocyclohexane hydrochloride was dissolved in 150 ml of water, and, then, 6.4 g of solid sodium hydroxide and 10.6 g of anhydrous sodium carbonate were added and dissolved. The solution was cooled in an ice bath to 10°. A solution containing 38.0 g of phthalyl- $\beta$ -alanyl chloride in 130 ml of dioxane was added dropwise to the solution with vigorous stirring by means of a blender. The temperature of the reaction mixture was maintained at 5-10° during the addition. After the addition had been completed, the white precipitates were filtered off, and washed with water. The crude product was recrystallized from boiling acetic acid. The white crystals which separated were collected, washed with ethanol and ether, and dried under vacuum. Yield, 28.3 g. *Anal.*, Calcd for C<sub>28</sub>H<sub>28</sub>N<sub>4</sub>O<sub>6</sub>: C, 65.09; H, 5.48; N, 10.85%. Found, C, 64.22; H, 5.79; N, 10.58%.

*N,N'*-Bis( $\beta$ -alanyl)-*R*-1,2-diaminocyclohexane hydrochloride. *N,N'*-Bis(phthalyl- $\beta$ -alanyl)-*R*-1,2-diaminocyclohexane (25.8 g, 0.05 mole) and hydrazine hydrate (5.0 g, 0.10 mole) were added to 500 ml of ethanol, and the mixture was heated under reflux for 4 hr. The subsequent treatments were the same as those mentioned in the case of the *R*-propylenediamine analogue. The product solidified by treating the residue with 20 ml of ethanol. This was filtered off, washed with ethanol and ether, and dried under vacuum. Yield, 6.1 g. This was used in a following reaction without further purification.

*N,N'*-bis( $\gamma$ -aminopropyl)-*R*-1,2-diaminocyclohexane. 6.1 g of *N,N'*-bis( $\beta$ -alanyl)-*R*-1,2-diaminocyclohexane hydrochloride was added to a suspension of lithium aluminium hydride (8.7 g) in tetrahydrofuran (200 ml). The mixture was heated under reflux for 24 hr with stirring. The subsequent treatments were the same as those described for the corresponding *R*-propylenediamine derivative. The yellow oily liquid, obtained after the removal of tetrahydrofuran, was used in the following reaction without further purification. The yield of the crude product is 3.80 g.

Trans-dichloro(*N,N'*-bis( $\gamma$ -aminopropyl)-*R*-1,2-diaminocyclohexane)cobalt(III) perchlorate (trans-[Co(*R*-apchn)Cl<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>). To the crude *R*-apchn (3.80 g) obtained as above, a solution of CoCl<sub>2</sub>·6H<sub>2</sub>O (3.58 g) in 30 ml of water was added in small portions. A small volume of concentrated HCl (about 0.5 ml) was added in order to dissolve the precipitates, which had appeared in the course of the above procedure. After the remaining precipitate had been filtered off, the filtrate was aerated for 5 hr. To the resultant solution, 5 ml of concentrated HCl was added, and, then, the solution was evaporated on a steam bath.

(17) R. G. Asperger and C. F. Liu, *Inorg. Chem.*, 4, 1492 (1965).

When a small amount of green crystals began to separate, 5 ml of 60% HClO<sub>4</sub> was added to the solution. The mixture was, then, cooled to room temperature, and the green crystals which separated were collected by filtration, washed with cold water, methanol and acetone, and air-dried. Yield, 2.00 g. It was recrystallized from dilute HCl. *Anal.*, Calcd for [Co(C<sub>12</sub>H<sub>28</sub>N<sub>4</sub>)Cl<sub>2</sub>]ClO<sub>4</sub>: C, 31.49; H, 6.17; N, 12.24%. Found: C, 31.65; H, 6.44; N, 11.98%.

$\Lambda$ - $\beta$ -oxalato(*N,N'*-bis( $\gamma$ -aminopropyl)-*R*-1,2-diaminocyclohexane)cobalt(III) perchlorate ( $\Lambda$ - $\beta$ -[Co(*R*-apchn)-ox]ClO<sub>4</sub>). A suspension of *trans*-[Co(*R*-apchn)Cl<sub>2</sub>]ClO<sub>4</sub> (0.92 g) and sodium oxalate (0.27 g) in 30 ml of water was heated on a steam bath. When the mixture turned to a red-colored solution, this was cooled in a refrigerator overnight. The red crystals, which separated, were filtered off, washed with cold water, methanol and acetone, and air-dried. Yield, 0.32 g. A further crop of the product could be recovered from the filtrate. *Anal.*, Calcd for [Co(C<sub>12</sub>H<sub>28</sub>N<sub>4</sub>)(C<sub>2</sub>O<sub>4</sub>)]ClO<sub>4</sub>: C, 35.41; H, 5.95; N, 11.80%. Found: C, 35.10; H, 5.89; N, 11.89%.

*dl*-2,3-Diaminobutane. It was prepared by the method of Balthis and Bailar.<sup>18</sup>

*Resolution of dl*-2,3-diaminobutane. This diamine was resolved by the method of Lucas *et al.*<sup>19</sup> After the removal of pure diastereomer salt of the *S* antipode, the impure diastereomer salt of the *R* antipode was collected, from which optically impure *R*-2,3-diaminobutane was recovered. The optical purity of this diamine was about 10%. It was used in the following reaction without further purification.

*N,N'*-bis(phthalyl- $\beta$ -alanyl)-(*R*)-2,3-diaminobutane. Partially resolved *R*-2,3-diaminobutane (7.30 g) and anhydrous potassium carbonate (11.5 g) were dissolved in 100 ml of water, and the solution was cooled in an ice bath. To the solution, a solution of phthalyl- $\beta$ -alanyl chloride (39.4 g) in 100 ml of dioxane was added dropwise with vigorous stirring by means of a blender, in a similar way as for the *R*-propylenediamine derivative. The product was filtered off, washed with water, and recrystallized from boiling acetic acid. Yield, 25.0 g. *Anal.* Calcd for C<sub>26</sub>H<sub>26</sub>N<sub>4</sub>O<sub>6</sub>: C, 61.39; H, 5.59; N, 11.02%. Found: C, 61.53; H, 5.56; N, 10.34%.

*N,N'*-bis( $\beta$ -alanyl)-(*R*)-2,3-diaminobutane hydrochloride. *N,N'*-bis(phthalyl- $\beta$ -alanyl)-(*R*)-2,3-diaminobutane (20.0 g) was treated with hydrazine hydrate (4.0 g) in the same way as that for the corresponding *R*-propylenediamine derivative. The subsequent procedures were also the same as those mentioned in the *R*-propylenediamine analogue. The yellow semi-solid mass, thus obtained, was used in the following reaction without further purification.

*N,N'*-bis( $\gamma$ -aminopropyl)-(*R*)-2,3-diaminobutane. *N,N'*-bis( $\beta$ -alanyl)-(*R*)-2,3-diaminobutane, obtained as above, was treated with lithium aluminium hydride

(14.0 g) in anhydrous tetrahydrofuran (280 ml) in a similar manner as that for the *R*-propylenediamine derivative. The subsequent treatments were also the same. The product was isolated by distillation, b.p. 151.5° (13 mm). Yield 3.0 g.

*Trans*-dichloro(*N,N'*-bis( $\gamma$ -aminopropyl)-(*R*)-2,3-diaminobutane)cobalt(III) perchlorate (*trans*-[Co(*R*-apbn)Cl<sub>2</sub>]ClO<sub>4</sub>). (*R*)-apbn (1.62 g), 1 N HCl (8 ml), and CoCl<sub>2</sub>·6H<sub>2</sub>O (1.90 g) were added to 50 ml of water, successively, and the resultant solution was aerated for 8 hr. To the resultant solution, 3 ml of concentrated HCl was added, and the solution was evaporated on a water bath to a volume of 10 ml. 5 ml of 60% HClO<sub>4</sub> was added to the resultant solution, and the green crystals which separated were filtered off, washed with ethanol and acetone, and air-dried. *Anal.* Calcd for [Co(C<sub>10</sub>H<sub>26</sub>N<sub>4</sub>)Cl<sub>2</sub>]ClO<sub>4</sub>: C, 27.82; H, 6.08; N, 12.98%. Found: C, 28.33; H, 6.29; N, 13.02%.

$\beta$ -Oxalato(*N,N'*-bis( $\gamma$ -aminopropyl)-(*R*)-2,3-diaminobutane)cobalt(III) perchlorate ( $\beta$ -[Co(*R*-apbn)ox]ClO<sub>4</sub>). A suspension of *trans*-[Co(*R*-apbn)Cl<sub>2</sub>]ClO<sub>4</sub> (0.43 g) and sodium oxalate (0.135 g) in 10 ml of water was heated on a steam bath. After a red-colored solution had been obtained, this was concentrated to a volume of 5 ml; the solution was, then, cooled to room temperature. The red crystals, which separated, were filtered off, washed with cold water, ethanol and ether, and air-dried. *Anal.* Calcd for [Co(C<sub>10</sub>H<sub>26</sub>N<sub>4</sub>)(C<sub>2</sub>O<sub>4</sub>)]ClO<sub>4</sub>: C, 31.11; H, 5.85; N, 12.49%. Found: C, 31.90; H, 5.90; N, 12.72%.

*Measurements.* The visible absorption spectra were obtained with a Shimadzu MPS-50L spectrophotometer. The circular dichroism spectra were measured with a JASCO J-20 automatic spectropolarimeter. The proton magnetic resonance spectra were obtained with a Hitachi R-20A spectrometer, and sodium 2,2-dimethyl-2-sila-pentanesulfonate was used as the internal reference.

## Results and Discussion

*Trans*-dichloro Complex. The dichlorocobalt(III) complex of *R*-apbn was obtained in a similar manner as for the 3,2,3-tet complex.<sup>8</sup> Green crystals were isolated as the perchlorate salt. The *trans* configuration with respect to the chlorides coordinated was established on the basis of the visible absorption spectrum. The absorption spectrum of the *R*-apbn complex is obviously similar to that of the *trans*-Co(3,2,3-tet)Cl<sub>2</sub><sup>+</sup> ion. The visible absorption and CD spectra of the *trans*-[Co(*R*-apbn)Cl<sub>2</sub>]ClO<sub>4</sub> and those of the (−)-*trans*-[Co(3,2,3-tet)Cl<sub>2</sub>]ClO<sub>4</sub> are shown in Figures 3 and 4, respectively. The CD curves of these complexes showed a dominant positive and a small negative bands in the region of 14,000-18,000 cm<sup>-1</sup>. These curves markedly resemble to each other.

The similarity in the CD curves between these complexes is considered to indicate the coincidence of the absolute configuration between the complexes. The most probable structure for the *R*-apbn complex

(18) I. H. Balthis and J. C. Bailar, *J. Amer. Chem. Soc.*, **74**, 944 (1952).

(19) F. H. Dickey, W. Fickett, and H. J. Lucas, *ibid.*, **81**, 4185 (1959).

is that shown in Figure 5, where the methyl group substituted at the central five membered chelate ring takes the  $\lambda$  conformation. The R-appn complex ion,

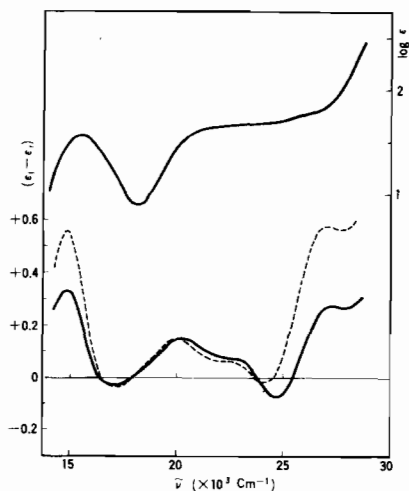


Figure 3. Visible absorption and CD spectra of  $trans\text{-Co(R-appn)Cl}_2^+$  ion (—), and CD spectrum of  $trans\text{-Co(R-apchn)Cl}_2^+$  ion (---).

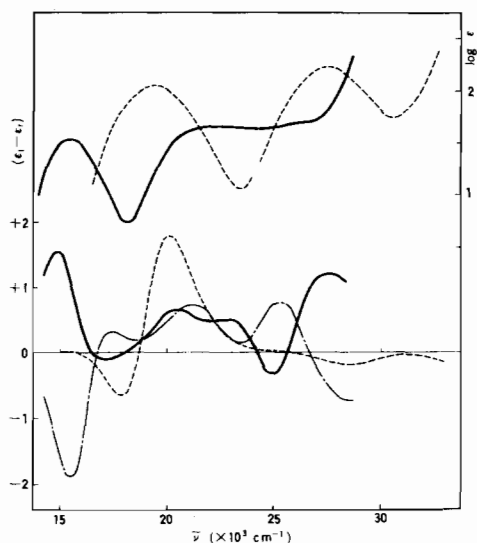


Figure 4. Visible absorption and CD spectra of  $(-)\text{-trans-Co(3,2,3-tet)Cl}_2^+$  ion (—) ( $\times 5$ ) and  $(+)\text{-Co(3,2,3-tet)ox}^+$  ion (---), and CD spectrum of  $trans\text{-Co((3S,8S)-dime-trien)Cl}_2^+$  ion -.-.-).

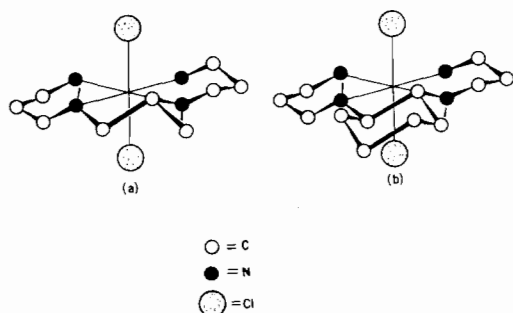


Figure 5. Probable structures of  $trans\text{-Co(R-appn)Cl}_2^+$  ion (a), and  $trans\text{-Co(R-apchn)Cl}_2^+$  ion (b).

shown here, takes the  $trans\text{-SS}$  configuration.

It has been observed that the  $trans\text{-dichlorocobalt(III)}$  complexes with a series of triethylenetetramine (trien) derivatives, which have methyl substituents, show the ORD and CD curves similar to one another.<sup>13,20</sup> Further, these curves are fundamentally identical with that of the active antipode of the corresponding trien complex.<sup>12</sup> This suggests that the vicinal contribution from the methyl group is negligibly small for the above complexes. A similar tendency has also been noticed for the dichlorocobalt(III)<sup>21,22</sup> and rhodium(III)<sup>23</sup> complexes with 1,2-diamines. The vicinal effect of the methyl group was, therefore, expected to be small in the case of the R-appn complex. Hence, the  $(-)_D$  enantiomer of  $trans\text{-Co(3,2,3-tet)Cl}_2^+$  ion should have the same configuration as that of the R-appn complex, since the former isomer showed a CD spectrum closely similar to that of the latter complex, as has been mentioned previously.

In the above assumption, the possibility that the methyl group adopts preferentially the axial orientation was not taken into consideration for the R-appn complex. If the methyl group of R-appn takes the axial orientation, the assignment given above must be altered. The possibility of the axially-situated methyl group was, in fact, suggested in some planar complexes with tetradentate Schiff base of R-propylenediamine.<sup>24</sup> In order to establish the orientation of the methyl group and the structure of the R-appn complex, we prepared  $N,N'$ -bis( $\gamma$ -aminopropyl)-R-1,2-diaminocyclohexane (= R-apchn), a derivative of R-1,2-diaminocyclohexane, and its dichlorocobalt(III) complex.

For the  $trans\text{-1,2-diaminocyclohexane}$  chelate ring, the conformational inversion can be ruled out because of its cyclic structure. The R antipode takes solely the  $\lambda$  conformation upon coordination. Therefore, the central chelate ring of the coordinated R-apchn must be fixed in the  $\lambda$  conformation. The structure of the  $trans\text{-Co(R-apchn)Cl}_2^+$  ion, deduced from the above consideration, is shown in Figure 5. The SS configuration is indicated with regard to the secondary N centers.

The CD spectrum of the  $trans\text{-[Co(R-apchn)Cl}_2\text{]ClO}_4$  are shown in Figure 3. The present CD curve obviously resembles that of the  $trans\text{-Co(R-appn)Cl}_2^+$  ion, though the peak height of each corresponding band is slightly varied to each other between these complexes, probably due to the difference in the vicinal effects between the cyclohexane ring and the methyl group. This means that the  $trans\text{-Co(R-appn)Cl}_2^+$  ion, as well as the  $trans\text{-Co(R-apchn)Cl}_2^+$  ion, surely has the SS configuration, as has been expected. Therefore, the  $(-)_D\text{-trans-Co(3,2,3-tet)Cl}_2^+$  ion, which shows a CD curve similar to that of the R-appn complex, should have the SS configuration. This means that the conclusion of Brubaker and Schaefer, which

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had assigned the RR configuration to the above 3,2,3-tet complex, must be altered with regard to the absolute configuration.

Brubaker and Schaefer had supposed the absolute configuration of the  $(-)_D$ -*trans*-Co(3,2,3-tet)Cl<sub>2</sub><sup>+</sup> ion on the basis of the pattern of the ORD curve of this complex, which was regarded to be similar to that of the  $(+)_D$ -*trans*-Co(trien)Cl<sub>2</sub><sup>+</sup> ion.<sup>10</sup> The latter complex had been determined to have the SS configuration.<sup>12</sup> The CD curve of the *trans*-Co((3S,8S)-dimetriene)Cl<sub>2</sub><sup>+</sup> ion ((3S,8S)-dimetriene = (3S,8S)-dimethyltriethylenetetramine), which adopts preferentially the *trans*-SS configuration, is given in Figure 4. It appeared from these CD curves in this Figure, that the complexes,  $(-)_D$ -*trans*-Co(3,2,3-tet)Cl<sub>2</sub><sup>+</sup> and *trans*-Co((3S,8S)-diemetriene)Cl<sub>2</sub><sup>+</sup> (or  $(+)_D$ -*trans*-Co(trien)Cl<sub>2</sub><sup>+</sup> ion), possess the opposed configuration to each other. Only the CD bands in the vicinity of 21,000 cm<sup>-1</sup> have the same signs for these ions. In practice, however, the above complex ions have commonly the *trans*-SS configuration. The conformation of the central ethylenediamine moiety is the same  $\lambda$  *gauche* form for these ions. The only structural difference between them is present in the outer chelate rings; the six-membered rings for the 3,2,3-tet complex, and five-membered rings for the trien complex. It must be noted, therefore, that a slight difference in ligands occasionally brings about marked differences in the behavior of CD of their metal complexes.

**Oxalato Complex.** The optically active form of the *trans*-Co(3,2,3-tet)Cl<sub>2</sub><sup>+</sup> complex had been derived from the optically active Co(3,2,3-tet)ox<sup>+</sup> ion (ox = oxalate ion), by treating the oxalato complex with dry hydrogen chloride gas in methanol.<sup>10</sup> The transformation from *cis* to *trans* geometry under this condition was considered to take place with retention of configuration with respect to the asymmetric secondary nitrogen centers. Because the  $(-)_D$  isomer of *trans*-Co(3,2,3-tet)Cl<sub>2</sub><sup>+</sup> ion has now been established to have the SS configuration, the precursor,  $(+)_S$ -Co(3,2,3-tet)ox<sup>+</sup> ion, should have the same SS configuration with regard to the coordinated secondary nitrogen centers. In conflict with this assignment, the  $(+)_S$  oxalato complex was considered to have the *cis*- $\alpha$ (RR) configuration by Brubaker *et al.*<sup>9,10</sup> Therefore, the oxalato complex of 3,2,3-tet seems to require some reexamination in its structure.

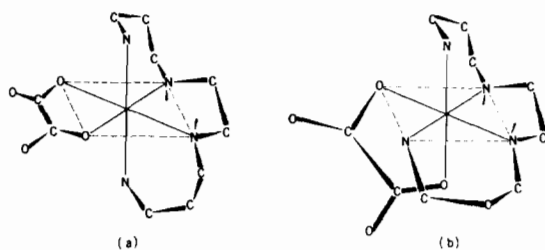


Figure 6. Probable structures of Co(3,2,3-tet)ox<sup>+</sup> ion; (a)  $\Delta$ - $\alpha$ (SS) and (b)  $\Lambda$ - $\beta$ (SS).

When the coordinated secondary nitrogen centers are restricted in the SS configuration, the probable

structures of the *cis* geometry of 3,2,3-tet complex are those shown in Figure 6. The chair conformation is adopted for the six-membered chelate rings. The possibility of the other *cis*- $\beta$  form, which has the RS combination of the secondary nitrogen atoms, was not taken into consideration in the present case. This geometry seems to be less stable, from the examination of a Dreiding stereo model, than the former two geometries. Further, it is unlikely that the *cis*- $\beta$ (RS) isomer gives rise to the *trans*-SS or -RR isomers under the acidic condition.

On this basis, either the  $\Delta$ - $\alpha$ (SS) or the  $\Lambda$ - $\beta$ (SS) geometry is probable for the  $(+)_S$ -Co(3,2,3-tet)ox<sup>+</sup> ion. If the absolute configuration can be estimated for this complex, the topology is readily determined. The  $\alpha$  topology should be appropriate for the  $\Delta$  absolute configuration, and the  $\beta$  for the  $\Lambda$  configuration.

The CD curve of the  $(+)_S$ -Co(3,2,3-tet)ox<sup>+</sup> ion shows a minor negative and a dominant positive bands in the first absorption band region (Figure 4). Brubaker and Schaefer have studied the CD of this ion, along with that of a series of other oxalato complexes.<sup>10</sup> They assigned these CD bands to the appropriate electronic transitions, and, moreover, estimated the absolute configuration of  $(+)_S$ -Co(3,2,3-tet)ox<sup>+</sup> ion based on the sign of the dominant CD band at about 20,500 cm<sup>-1</sup>. This enantiomer was assigned the  $\Lambda$  absolute configuration. If the assignment was exactly made, the  $(+)_S$ -Co(3,2,3-tet)ox<sup>+</sup> ion must have the  $\Lambda$ - $\beta$ (SS) configuration.

In order to confirm the topology of the Co(3,2,3-tet)ox<sup>+</sup> complex, we prepared N,N'-bis( $\gamma$ -aminopropyl)-*dl*-2,3-diaminobutane (= apbn) and its oxalato complex, together with the oxalato complexes of R-apbn and R-apchn. The ligand, apbn, employed in this study, contains a slight excess of R-antipode (the optical purity is about 10%). This is due to the purity of the *dl*-2,3-diaminobutane used as a starting material, which was occasionally available as the remainder from the isolation of the pure S antipode. Therefore, this tetradentate ligand will be represented as (R)-apbn, hereafter, and distinguished from the pure antipode, R-apbn.

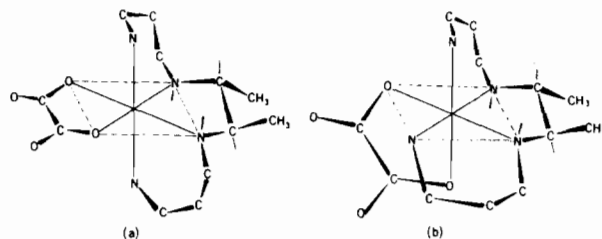


Figure 7. Probable structures of Co(R-apbn)ox<sup>+</sup> ion; (a)  $\Delta$ - $\alpha$ (SS) and (b)  $\Lambda$ - $\beta$ (SS).

The probable structures of the Co(R-apbn)ox<sup>+</sup> ion (R-apbn refers to the pure enantiomer),  $\Delta$ - $\alpha$ (SS) and  $\Lambda$ - $\beta$ (SS) form, are represented in Figure 7. As far as the two methyl groups locate in the equatorial orientation, and the central chelate ring adopts the  $\lambda$  conformation, only these structures are possible for

the *cis* geometry. In the  $\Delta\text{-}\alpha(\text{SS})$  form, two methyl groups can be regarded as identical; in the  $\Delta\text{-}\beta(\text{SS})$  form, however, they are situated in the intrinsically different circumstances. The measurement of the proton magnetic resonance (pmr) spectrum of  $\text{Co}((\text{R})\text{-apbn})\text{ox}^+$  ion must serve to determine whether  $\Delta\text{-}\alpha(\text{SS})$  or  $\Delta\text{-}\beta(\text{SS})$  is the actual configuration of this ion. If the complex takes the  $\Delta\text{-}\alpha(\text{SS})$  configuration, the pmr signals for the methyl groups should be observed as only one doublet. On the other hand, the methyl signals would be, in principle, observed as two doublets of the equal intensity for the  $\Delta\text{-}\beta(\text{SS})$  configuration.

However, there is a significant subject to be solved before the inspection of the pmr spectrum of  $\text{Co}((\text{R})\text{-apbn})\text{ox}^+$  ion. That is whether the 3,2,3-tet analogues with the equatorial substituent(s) at the central diamine chelate ring coordinate in the topological way identical with the non-substituted 3,2,3-tet or not. For the purpose of investigating this problem, the CD curves of the oxalato complex with 3,2,3-tet derivatives were examined.

It is most probable that, for R-apbn and R-apchn, the conformation of the central chelate ring is restricted in the  $\lambda$  *gauche* form even in the *cis* geometry. Further, the *cis* complexes with these ligands should adopt the SS configuration with respect to the secondary nitrogen centers. This is consistent with the fact that the conformation of the central five-membered chelate rings for the probable structures of  $\text{Co}(3,2,3\text{-tet})\text{ox}^+$  ion (the SS configuration, cf Figure 6) have the  $\lambda$  *gauche* forms. Therefore, the probable structure for the oxalato complexes of R-apbn and R-apchn should be either  $\Delta\text{-}\alpha(\text{SS})$  or  $\Delta\text{-}\beta(\text{SS})$ .

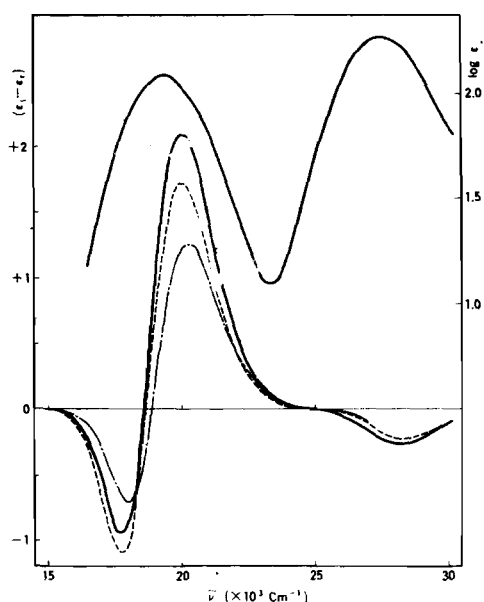


Figure 8. CD curves of  $\text{Co}(\text{R-apbn})\text{ox}^+$  ion (—),  $\text{Co}(\text{R-apchn})\text{ox}^+$  ion (---), and  $\text{Co}(\text{R})\text{-apbn})\text{ox}^+$  ion ( $\times 10$ ) (— · —), and Visible absorption curve of  $\text{Co}(\text{R-apbn})\text{ox}^+$  ion (—).

The CD curves of the  $\text{Co}(\text{R-apbn})\text{ox}^+$  and  $\text{Co}(\text{R-apchn})\text{ox}^+$  ions are shown in Figure 8. These cur-

ves are similar to each other and, moreover, to that of the  $(+)\text{Co}(3,2,3\text{-tet})\text{ox}^+$  ion. This suggests not only that the R-apbn and R-apchn complexes have the same absolute configuration as the  $(+)\text{Co}(3,2,3\text{-tet})\text{ox}^+$  complex, but also that the former adopt the topology identical with the latter. It was indicated, therefore, that the equatorial substituents at the central chelate ring exhibit no influence in determining the topology of *cis* geometry in the case of 3,2,3-tet derivatives. Hence, it was expected that the oxalato complex of (R)-apbn should have the same topology as those of R-apbn, R-apchn and 3,2,3-tet.

Therefore, the  $\text{Co}(\text{R-apbn})\text{ox}^+$  complex, if obtained, must show a CD curve similar to those of the R-apbn and R-apchn complexes. The  $\text{Co}((\text{R})\text{-apbn})\text{ox}^+$  complex is available as the substitute for the pure R-apbn complex, because the optical activity observed for the (R)-apbn complex must be attributed to the excess enantiomer of the used ligand, that is, the R antipode. The CD curve of this complex is given in Figure 8. (The CD curve shown here is that enlarged at 10 times the original one). Although the intensity of each CD band is lower than the other complexes, reflecting the low optical purity of the ligand, the behavior of this CD curve is, on the whole, markedly similar to the others. The similarity in CD between the (R)-apbn complex and the R-apbn complex and others indicates the identity of the topology between the complexes, as expected previously.

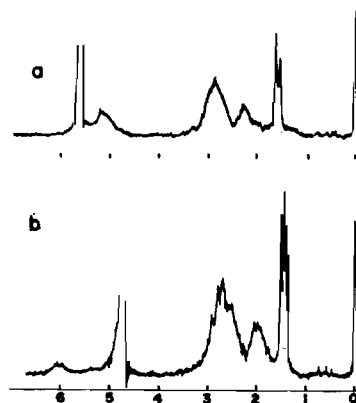


Figure 9. pmr spectra of (a)  $\text{trans-Co}((\text{R})\text{-apbn})\text{Cl}_2^+$  ion, and (b)  $\text{Co}((\text{R})\text{-apbn})\text{ox}^+$  ion.

The pmr spectrum of the  $\text{Co}((\text{R})\text{-apbn})\text{ox}^+$  ion is shown in Figure 9, along with that of the precursor,  $\text{trans-Co}((\text{R})\text{-apbn})\text{Cl}_2^+$  ion. The methyl signals are observed as only one doublet for the latter complex, as expected, since, in *trans* geometry, two methyl groups of the ligand should be situated in the identical environments. On the contrary, the methyl signals are observed as two doublets of the equal intensity for the oxalato complex. This means that the present complex certainly adopts the  $\beta$  topology.

Consequently, the  $\text{Co}(\text{R-apbn})\text{ox}^+$ ,  $\text{Co}(\text{R-apchn})\text{ox}^+$ , and  $(+)\text{Co}(3,2,3\text{-tet})\text{ox}^+$  complex ions, which must have the same topology as the (R)-apbn complex, are determined to adopt the  $\Delta\text{-}\beta(\text{SS})$  configuration. This

is consistent with the assumption, which has been mentioned previously for the  $(+ {}_{516}\text{-Co}(3,2,3\text{-tet})\text{ox}^+$  ion, based on the sign of the dominant CD band. Thus, it is established that the oxalato complexes of

3,2,3-tet and its derivatives have the *cis*- $\beta$  configuration. The previous description that the oxalato complex of 3,2,3-tet has the *cis*- $\alpha$  configuration is considered to be mistaken.