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# Metal Complexes Containing Six-membered Chelate Rings V. Preparation and Structure of Oxalato Complexes of Cobalt(III) with Substituted 3,7-Diaza-1,9-nonanediamine Derived from 2,4-Pentanediamine1)

Fujio Mizukami*

*Department of Chemistry, Faculty of Science, Tohoku University, Aoba, Aramaki, Sendai 980*

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The syntheses, resolution and structure of three oxalato complexes of cobalt (III) with tetramine ligand, *R*(4), *R*(6)- and *R*(4), *S*(6)-4,6-dimethyl-1,9-nonanediamine (*RR*- and *RS*-2,3″, 2-tet), and *R*(6), *S*(8)-6,8-dimethyl-2,5,9,12-tetraazatridecane ($N,N'$-$Me_2$-*RS*-2,3″,2-tet) are reported. Only one geometrical isomer (*cis* $\beta$) was isolated for each complex, [Co(ox)($N,N'$-$Me_2$-*RS*-2,3,″,2-tet)]$^+$, [Co(ox)(*RS*-2,3″,2-tet)]$^+$ and [Co(ox)(*RR*-2,3″,2-tet)]$^+$. The central six-membered chelate rings of $(-)_{546}$-*cis* $\beta$-[Co(ox)($N,N'$-$Me_2$-*RS*-2,3″,2-tet]$^+$ and $(-)_{546}$-*cis* $\beta$-[Co-(ox)(*RS*-2,3″,2-tet)]$^+$ take a chair conformation with two equatorial methyl groups, and that of $(-)_{546}$-*cis* $\beta$-[Co-(ox)(*RR*-2,3″,2-tet)]$^+$ a chair conformation with an axial and equatorial methyl group.

Studies have been carried out on cobalt(III) complexes of 2,4-pentanediamine, a $\beta$-diamine with a methyl group on each $\alpha$-carbon atom of trimethylenediamine.2–5) Transition metal complexes containing 3,7-diaza-1,9-nonanediamine (2,3,2-tet) were investigated by Hamilton and Alexander and others.6–14) However, few stereochemical studies have been carried out on the cobalt(III) complexes of tetramine involving a substituted trimethylenediamine part.15) Complexes of cobalt(III) with 2,3,2-tet derivatives containing 2,4-pentanediamine part were prepared in order to elucidate the correlations between the configuration of asymmetric carbon and nitrogen atom, the conformation of the chelate ring, and the configuration about metal ion.

Only one isomer (*trans*) was isolated for each dichloro complex of cobalt(III) with tetramine ligand, *R*(4), *R*(6)- and *R*(4), *S*(6)-4,6-dimethyl-3,7-diaza-1,9-nonanediamine (*RR*- znd *RS*- 2,3″,2-tet) and *R*(6), *S*(8)-6,8-dimethyl-2,5,9,12-tetraazatridecane ($N,N'$-$Me_2$-*RS*-2,3″,2-tet).1) This paper deals with the preparation of *cis* oxalato complexes of cobalt(III) each with tetramine,$N,N'$-$Me_2$-*RS*-2,3″,2-tet, *RS*-2,3″,2-tet and *RR*-2,3″,2-tet, and their stereochemistry on the basis of CD and PMR spectra.

## Experimental

R*(4),*R*(6)-, and* R*(4),*S*(6)-4,6-dimethyl-3,7-diaza-1,9-nonanediamine (*RR*-2,3″,2-tet and* RS*-2,3″,2-tet) and* R*(6),*S*(8)-6,8-dimethyl-2,5,9,12-tetraazatridecane (*N,N′*-Me*$_2$-RS*-2,3″,2-tet)*: Prepared according to the method described previously.1)

trans-*[CoCl$_2$(*RR*-2,3″,2-tet)]ClO$_4$,* trans-*[CoCl$_2$(*RS*-2,3″,2-tet)]ClO$_4$ and* trans-*[CoCl$_2$(*N,N′-*Me$_2$-*RS*-2,3″,2-tet)]ClO$_4$*: Prepared according to the reported method.1)

*$(-)_{546}$-*cis$\beta$*-[Co(ox)(*RR*-2,3″,2-tet)]ClO$_4$*: A solution containing 0.7 g of *trans*-[CoCl$_2$(*RR*-2,3″,2-tet)]ClO$_4$ and 0.4 g of sodium oxalate in 40 ml of water was warmed at 65—70 °C for 2 hr. After being cooled to room temperature, the red crystals (I) were filtered off and washed with a small amount of cold water. The filtrate and washing were combined and concentrated to 10 ml in a vacuum desiccator over phosphorus pentoxide. A second crop of red crystals (II) was filtered off and washed with a small amount of cold water. Crystal II was found to be the same as crystal I on the basis of absorption, CD and PMR spectra. The crystals were recrystallized by evaporating the aqueous solution in a vacuum desiccator over phosphorus pentoxide. Yield: 0.6 g. Found: C, 30.44; H, 5.82; N, 12.91%. Calcd for $C_{11}H_{24}N_4ClO_8Co$: C, 30.39; H, 5.56; N, 12.89%.

*Racemic-*cis$\beta$*-[Co(ox)(*RS*-2,3″,2-tet)]ClO$_4$·H$_2$O*: This was prepared from *trans*-[CoCl$_2$(*RS*-2,3″-2-tet)]ClO$_4$ (1.5 g) and sodium oxalate (0.5 g) by a similar method to that for corresponding *RR*-2,3,2-tet complex described above. Yield: 1.15 g. Found: C, 29.17; H, 6.24; N, 12.82%. Calcd for $C_{11}H_{26}N_4ClO_9Co$: C, 29.18; H, 5.79; N, 12.38%.

*$(-)_{546}$-*cis$\beta$*-[Co(ox)(*RS*-2,3″,2-tet)]$^+$ Complex*: To a stirred solution of racemic-*cis$\beta$*-[Co(ox)(*RS*-2,3″,2-tet)]ClO$_4$·H$_2$O (1 g) in 100 ml of water at 70 °C was added slowly 0.9 g of sodium hydrogen dibenzoyltartrate in 50 ml of hot water. After *ca.* two hr, the solution was evaporated to 50 ml at 70 °C under reduced pressure and cooled to room temperature. A deposited pink powder was filtered off. The powder was suspended in 50 ml of water at 60 °C, stirred for 30 min, and then filtered off. The insoluble material was treated further twice with warm water in the same way. The residue was dissolved in an appropriate amount of 10% perchloric acid, and gradually evaporated to remove less soluble dibenzoyltartaric acid and racemic-*cis$\beta$*-[Co(ox)(*RS*-2,3″,2-tet)]ClO$_4$·H$_2$O which were filtered off occasionally. Evaporation was continued until the ratio of $\Delta\varepsilon$ and $\varepsilon$ values of the filtrate became constant. More soluble, optically active, crystalline perchlorate was obtained from the final filtrate. However, it was contaminated with dibenzoyltartaric acid which could not be removed completely. Thus, the quantitative CD curve of $(-)_{546}$-*cis$\beta$*-[Co(ox)(*RS*-2,3″,2-tet)]$^+$ was determined by the aid of the $\varepsilon$ values of racemate.

*Racemic-*cis$\beta$*-[Co(ox)(*N,N′-*Me$_2$-*RS*-2,3″,2-tet)]ClO$_4$·H$_2$O*: A solution containing 1.2 g of *trans*-[CoCl$_2$($N,N'$-$Me_2$-*RS*-2,3″,2-tet)]ClO$_4$ and 0.36 g of sodium oxalate was warmed at 70 °C for 6 hr, and filtered while hot. The filtrate was cooled to room temperature and evaporated to 4 ml under reduced pressure in a vacuum desiccator over phosphorus pentoxide. The deposited crystals were filtered off, washed with a small amount of cold water and ethanol, and air-dried. The crystals were recrystallized from a small amount of hot water. Yield: 1.1 g. Found: C, 32.79; H, 6.56; N, 11.41%. Calcd for $C_{13}H_{30}N_4ClO_9Co$: C, 32.48; H, 6.29; N, 11.65%.

*$(-)_{546}$- and $(+)_{546}$-*cis$\beta$*-[Co(ox)(*N,N′-*Me$_2$-RS-2,3″,2-tet)]ClO$_4$*: Half a gram of racemic-*cis$\beta$*-[Co(ox)($N,N'$-$Me_2$-2,3″,2-tet)]ClO$_4$·H$_2$O was dissolved in 70 ml of water at 70 °C. To the solution was added slowly 1 g of sodium hydrogen

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* Present Address, National Chemical Laboratory for Industry (Tokyo Kogyo Shikensho), 1-1-5, Honmachi, Shibuya-ku, Tokyo 151.

dibenzoyltartrate in 50 ml of hot water and stirred for 1 hr. After being cooled to room temperature, a pink powder was filtered off to give crude dibenzoyltartrate salt of $(-)_{546}$-isomer. The filtrate was stored to obtain $(+)_{546}$-isomer. The powder dissolved in an appropriate amount of 10% perchloric acid at 65 °C and cooled to room temperature. The deposited crystals of dibenzoyltartaric acid were filtered off and the filtrate was allowed to stand for a while. The crude perchlorate of $(-)_{546}$-isomer was filtered off and recrystallized from water fractionally until the CD showed a constant curve. The filtrate free of pink powder was evaporated to 50 ml at 60 °C. To the solution was added slowly an appropriate amount of 60% perchloric acid and cooled to room temperature. The deposited crystals of dibenzoyltartaric acid were filtered off and the filtrate was allowed to stand for a while. The crude perchlorate of $(+)_{546}$-isomer was filtered off and recrystallized from water fractionally until the CD of $(+)_{546}$-isomer became constant. The pure optically active perchlorate is less soluble in water than the racemate. Found: C, 33.56; H, 6.59; N, 11.78%. Calcd for $C_{11}H_{24}N_4ClO_8Co$: C, 33.74; H, 6.10; N, 12.11%.

*Measurements.* Visible and ultraviolet absorption spectra were obtained with a Hitachi 124 recording spectrophotometer. The CD curves were recorded with a Model ORD/UV-5 JASCO spectrophtometer with a CD attachment. PMR spectra in $D_2O$ were obtained with a Varian T-60 spectrometer using Na–TMS as an internal standard. The perchlorate salts of $(-)_{546}$-*cisβ*[Co(ox)(*RR*-2,3″,2-tet)]$^+$ and $(-)_{546}$-*cisβ*-[Co(ox)(*N*,*N*′-Me$_2$-*RS*-2,3″,2-tet)]$^+$ were converted into chloride salts by use of the anion exchanger Dowex 1-X4 in chloride form. $(-)_{546}$-*cisβ*-[Co(ox)(*RS*-2,3″,2-tet)]ClO$_4$·H$_2$O was converted into sulphate by treating with potassium sulphate, because of poor solubility of these complexes in $D_2O$. All the measurements were carried out at room temperature.

## Results and Discussion

*Structures of Complexes.* Two geometrical isomers are possible for the oxalatotetramine complexes of cobalt(III). In the present study, however, only one could be isolated for [Co(ox)(*N*,*N*′-Me$_2$-*RS*-2,3″,2-tet)]$^+$, [Co(ox)(*RS*-2,3″,2-tet)]$^+$, and [Co(ox)(*RR*-2,3″,2-tet)]$^+$. Each complex was fractionally crystallized as a perchlorate salt, all the fractions being spectrophotometrically identical and giving the same pattern in the PMR spectra. Accordingly, the geometrical configuration for [Co(ox)(*N*,*N*′-Me$_2$-*RS*-2,3″,2-tet)]$^+$, [Co(ox)(*RS*-2,3″,2-tet)]$^+$ and [Co(ox)(*RR*-2,3″,2-tet)]$^+$ should be assigned to *cisα* or *cisβ*.

For [Co(ox)(*N*,*N*′-Me$_2$-*RS*-2,3″,2-tet)]$^+$, molecular models indicate that *cisα* isomer is a less stable form than *cisβ* in which the two *C*-methyl groups locate in the equatorial orientation and the central chelate ring takes a chair conformation (Table 1). For the *cisβ* form, four isomers can exist with respect to the orientation of the two *N*-methyl groups. Of the isomers, the form in which one methyl group on the in-plane nitrogen atom takes an axial orientation to the terminal five-membered chelate ring and the other on the out-plane nitrogen atom exists in an equatorial position to another terminal five-membered chelate ring, seems to involve smaller steric interaction than the other forms. Accordingly, [Co(ox)(*N*,*N*′-Me$_2$-*RS*-2,3″,2-tet)]$^+$ seems to be assigned to an enantiomeric pair of the structure (Fig. 1–a). The PMR spectrum of $(-)_{546}$-[Co(ox)(*N*,*N*′-Me$_2$-*RS*-2,3″,2-tet)]$^+$ is consistent with this assignment since two doublets at 1.2—2.2 ppm and two singlets at 2.2 ppm and 3.2 ppm are assigned to two kinds of *C*-methyl group and two kinds of *N*-methyl group, respectively (Fig. 3–b).

Table 1. Conformations of 2,4-pentanediamine part in tetramines

| Ligand | Conformation Chair | δ-skew-boat | λ-skew-boat |
|---|---|---|---|
| *RR*-2,3″,2-tet | a, e | a, a | e, e |
| *RS*-2,3″,2-tet | a, a  e, e | a, e | a, e |
| *N*,*N*′-Me$_2$-*RS*-2,3″,2-tet | a, a  e, e | a, e | a, e |

a: methyl axial  e: methyl equatorial.

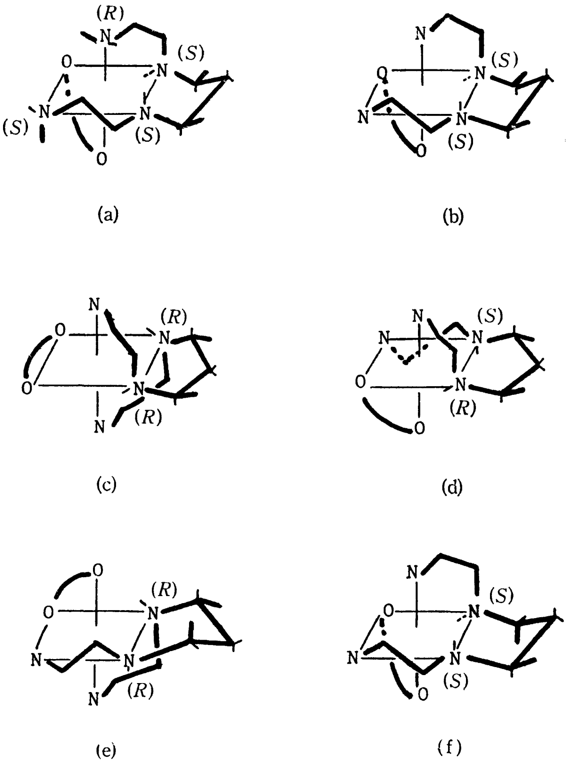

Fig. 1. Schematic structures of *cis*-[Co(ox)(2,3″,2-tet)]$^+$
( a ) *Λ*-*cisβ*-*N*(*S*),*N*(*S*),*N*(*S*),*N*(*R*)-[Co(ox)(*N*,*N*′-Me$_2$-*RS*-2,3″,2-tet)]$^+$
( b ) *Λ*-*cisβ*-*N*(*S*),*N*(*S*)-[Co(ox)(*RS*-2,3″,2-tet)]$^+$
( c ) *Λ*-*cisα*-*N*(*R*),*N*(*R*)-[Co(ox)(*RR*-2,3″,2-tet)]$^+$
( d ) *Δ*-*cisβ*-*N*(*R*),*N*(*S*)-[Co(ox)(*RR*-2,3″,2-tet)]$^+$
( e ) *Δ*-*cisβ*-*N*(*R*),*N*(*R*)-[Co(ox)(*RR*-2,3″,2-tet)]$^+$
( f ) *Λ*-*cisβ*-*N*(*S*),*N*(*S*)-[Co(ox)(*RR*-2,3″,2-tet)]$^+$

The CD spectra of the complexes prepared here are similar to the spectrum of $(+)_{546}$-*cisβ*-[Co(ox)(2,3,2-tet)]$^+$, which is assiged *Λ* configuration and in which the central six-membered chelate ring takes a chair conformation[9–11] (Fig. 2, Table 2). Similarity between the CD spectra of the four complexes strongly suggests that these complexes belong to the same chilarity. Thus, $(-)_{546}$-[Co(ox)(*N*,*N*′-Me$_2$-*RS*-2,3″,2-tet)]$^+$ should be assigned to the structure, *Λ*-*cisβ*-*N*(*S*), *N*(*S*), *N*(*S*), *N*(*R*)-[(*δ-gauche*)(chair),(*δ-gauche*)] (Fig.

TABLE 2. NUMERICAL DATA OF ABSORPTION (AB) AND CIRCULAR DICHROISM (CD) $\tilde{\nu}$ IN $10^3$ cm$^{-1}$, (log $\varepsilon$) AND ($\varepsilon_l - \varepsilon_r$)

| Complex | AB | CD |
|---|---|---|
| (−)$_{546}$-*cisβ*-[Co(ox)(*RR*-2,3″,2-tet)]ClO$_4$ | 19.80 (2.16) | 18.42 (+2.34) |
| | | 20.62 (−1.27) |
| | 27.55 (2.24) | *ca.* 25.97 (+0.27) |
| | | 28.41 (+0.43) |
| | | 32.26 (−0.03) |
| | 43.10 (4.39) | 39.06 (+3.44) |
| | | 46.08 (−22.39) |
| (−)$_{546}$-*cisβ*-[Co(ox)(*RS*-2,3″,2-tet)]ClO$_4$·H$_2$O | 10.92 (2.12) | 18.48 (+1.68) |
| | | 20.75 (−0.90) |
| | | 25.64 (+0.04) |
| | 28.09 (2.27) | 28.99 (+0.23) |
| | 42.55 (4.34) | |
| (−)$_{546}$-*cisβ*-[Co(ox)(*N*,*N*′-Me$_2$-*RS*-2,3″,2-tet)]ClO$_4$ | 19.23 (2.08) | 18.18 (+1.56) |
| | | 20.20 (−0.84) |
| | 26.95 (2.22) | 25.00 (+0.10) |
| | | 28.17 (+0.07) |
| | | 32.79 (−0.19) |
| | | 36.50 (+0.83) |
| | 41.15 (4.38) | 45.05 (−19.33) |

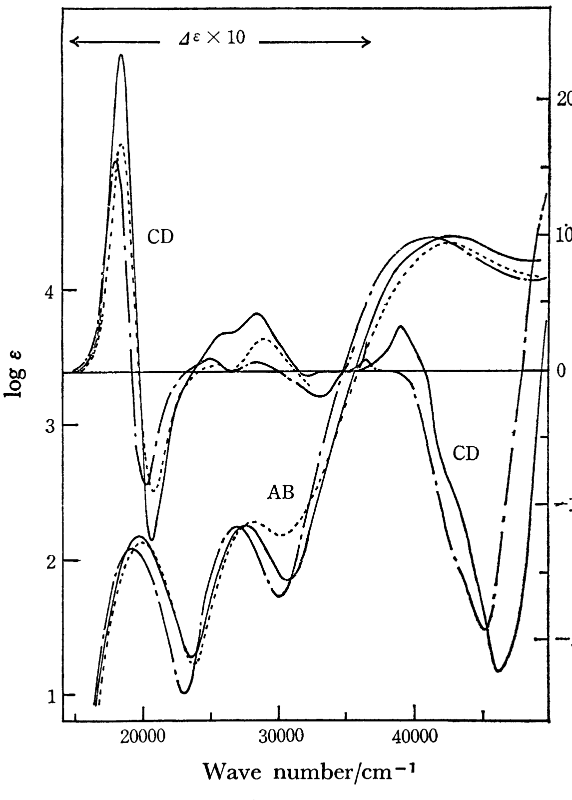

Fig. 2. Absorption (AB) and CD spectra of
(——) (−)$_{546}$-*cisβ*-[Co(ox)(*RR*-2,3″,2-tet)]ClO$_4$
(----) (−)$_{546}$-*cisβ*-[Co(ox)(*RS*-2,3″,2-tet)]ClO$_4$·H$_2$O
(—·—) (−)$_{546}$-*cisβ*-[Co(ox)(*N*,*N*′-Me$_2$-*RS*-2,3″,2-tet)]-ClO$_4$ in H$_2$O.

1-a). This was substantiated by X-ray analysis of the crystalline (−)$_{546}$-[Co(ox)(*N*,*N*′-Me$_2$-*RS*-2,3″,2-tet)]ClO$_4$.[16]

(−)$_{546}$-[Co(ox)(*RS*-2,3″,2-tet)]$^+$ gives a CD curve similar to that of *Λ*-(−)$_{546}$-*cisβ*-[Co(ox)(*N*,*N*′-Me$_2$-*RS*-2,3″,2-tet)]$^+$ (Fig. 2). The *RS*-2,4-pentadiamine part of *RS*-2,3″,2-tet tends to take a chair conformation in the complex of cobalt(III) because of the steric regulation coming from the methyl groups in the six-membered chelate ring (Table 1).[1–5] The PMR spectrum of (−)$_{546}$-[Co(ox)(*RS*-2,3″,2-tet)]$^+$ is shown in Fig. 3-a. Two doublets at 1.4 ppm are assigned to two kinds of methyl signal. This seems to support the view that [Co(ox)(*RS*-2,3″,2-tet)]$^+$ takes *cisβ* configuration. Thus, (−)$_{546}$-[Co(ox)(*RS*-2,3″,2-tet)]$^+$ is assigned to the structure, *Λ*-*cisβ*-*N*(*S*), *N*(*S*)-[(*δ*-*gauche*)(chair)-(*δ*-*gauche*)] (Fig. 1-b).

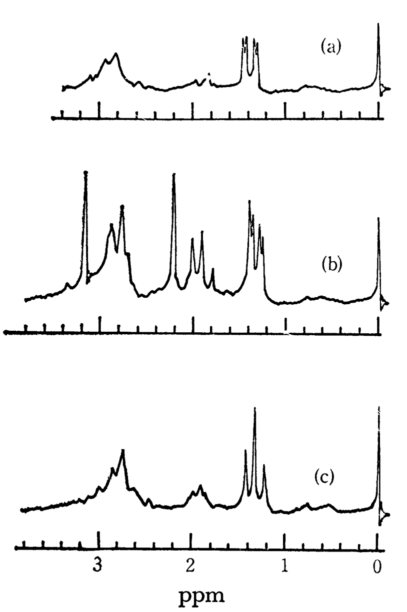

Fig. 3. PMR spectra of
(a) (−)$_{546}$-*cisβ*-[Co(ox)(*RS*-2,3″,2-tet)]$_2$SO$_4$
(b) (−)$_{546}$-*cisβ*-[Co(ox)(*N*,*N*′-Me$_2$-*RS*-2,3″,2-tet)]Cl
(c) (−)$_{546}$-*cisβ*-[Co(ox)(*RR*-2,3″,2-tet)]Cl in D$_2$O.

For the complex of (−)$_{546}$-[Co(ox)(*RR*-2,3″,2-tet)]$^+$, the central six-membered chelate ring adopts $\lambda$ skew-boat conformation (Table 1) as long as the two methyl groups locate in the equatorial orientation. In this case, the probable structure of (−)$_{546}$-[Co(ox)(*RR*-2,3″,2-tet)]$^+$ are *Δ*-*cisβ*-*N*(*R*), *N*(*S*) and *Λ*-*cis* *α*-*N*(*R*), *N*(*R*) form (Figs. 1-c and 1-d). In the former structure, the two methyl groups are non-equivalent to each other, whereas, in the latter structure, they are equivalent to each other. If the central six-membered chelate ring forms a chair conformation, one methyl group locates in the equatorial orientation and the other takes axial position (Table 1). In this case, both structures *Δ*-*cisβ*-*N*(*R*), *N*(*R*) and *Λ*-*cisβ*-*N*(*S*), *N*(*S*) are possible for [Co(ox)(*RR*-2,3″,2-tet)]$^+$ (Figs. 1-e and 1-f). In these structure, the two methyl groups are non-equivalent to each other.

The CD spectrum of (−)$_{546}$-[Co(ox)(*RR*-2,3″,2-tet)]$^+$ is similar to that of *Λ*-(−)$_{546}$-*cisβ*-[Co(ox)(*N*,*N*′-Me$_2$-

*RS*-2,3″,2-tet)]$^+$ whose absolute configuration was determined by the X-ray method (Fig. 2).[16] Thus, [Co(ox)(*RR*-2,3″,2-tet)]$^+$ should be assigned to $\Lambda$-*cisα*-*N*(*R*), *N*(*R*) or $\Lambda$-*cisβ*-*N*(*S*), *N*(*S*) structure. The PMR spectrum of $(-)_{546}$-[Co(ox)(*RR*-2,3″,2-tet)]$^+$ gives a triplet signal which seems to be an accidental overlapping of two doublet signals due to the two methyl groups (Fig. 3-c). Thus, $(-)_{546}$-[Co(ox)(*RR*-2,3″,2-tet)]$^+$ is assigned to the structure, $\Lambda$-*cisβ*-*N*(*S*), *N*(*S*)-[(*δ*-*gauche*)(chair)(*δ*-*gauche*)] (Fig. 1-f). The validity of this assignment was established by the X-ray method.[17]

The [Co(ox)(*RR*-2,3″,2-tet)]$^+$ was prepared by the reaction of $[\mathrm{Co(ox)_3}]^{3-}$ and *RR*-2,3″,2-tet. The obtained crystals also have $\Lambda$-$(-)_{546}$-*cisβ*-*N*(*S*), *N*(*S*) form as assigned above. These results lead to the conclusion that the $\Lambda$-$(-)_{546}$-*cisβ*-*N*(*S*),*N*(*S*) -[Co(ox)(*RR*-2,3″,2-tet)]$^+$ could be prepared stereospecifically.

*Absorption Spectra.* The absorption spectra of three oxalatotetramine cobalt(III) complexes are compared in Table 2 and Fig. 2. The absorption bands including the first and second band are shifted from longer to shorter wavelength, *i.e.* in the order $(-)_{546}$-*cisβ*-[Co(ox)(*N*,*N*′-Me$_2$-*RS*-2,3″,2-tet)]$^+$ $(-)_{546}$-*cisβ*-[Co(ox)(*RR*-2,3″,2-tet)]$^+$ and $(-)_{546}$-*cisβ*-[Co(ox)(*RS*-2,3″,2-tet)]$^+$. This is in line with the fact that the absorption bands of *trans*-[CoCl$_2$(*N*,*N*′-Me$_2$-*RS*-2,3″,2-tet)]$^+$ are shifted to longer wavelength compared with those *trans*-[CoCl$_2$(*RR*-2,3″,2-tet)]$^+$ and *trans*-[CoCl$_2$(*RS*-2,3″,2-tet)]$^+$.[1] At present, it is difficult to explain why the absorption bands of $(-)_{546}$-*cisβ*-[Co(ox)(*RR*-2,3″,2-tet)]$^+$ are shifted to longer wavelength than those of $(-)_{546}$-*cisβ*-[Co(ox)(*RS*-2,3″,2-tet)]$^+$. However, this result seems to be related to the structural stabilities of these complexes, since $\Lambda$-$(-)_{546}$-*cisβ*-*N*(*S*), *N*(*S*)-[Co(ox)(*RR*-2,3″,2-tet)]$^+$ with an axial and equatorial methyl group is less stable than $\Lambda$-$(-)_{546}$-*cisβ*-*N*(*S*), *N*(*S*)-[Co(ox)(*RS*-2,3″,2-tet)]$^+$ with two equatorial methyl groups.

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## References

1) Part IV of this series, F. Mizukami, This Bulletin, in press.

2) F. Mizukami, H. Ito, J. Fujita, and K. Saito, This Bulletin, **44**, 3051 (1971).

3) F. Mizukami, H. Ito, J. Fujita, and K. Saito, *ibid.*, **45**, 2129 (1972).

4) F. Mizukami, H. Ito, J. Fujita, and K. Saito, *ibid.*, **46**, 2410 (1973).

5) A. Kobayashi, F. Marumo, Y. Saito, J. Fujita, and F. Mizukami, *Inorg. Nucl. Chem. Lett.*, **7**, 777 (1971).

6) H. G. Hamilton, Jr. and M. D. Alexander, *Inorg. Chem.*, **5**, 2060 (1966).

7) H. G. Hamilton, Jr. and M. D. Alexander, *J. Amer. Chem. Soc.*, **89**, 5066 (1967).

8) P. C. Harrington, S. Linke, and M. D. Alexander, *Inorg. Chem.*, **12**, 168 (1973).

9) G. R. Brubaker and D. P. Schaefer, *ibid.*, **9**, 2372 (1970).

10) G. R. Brubaker and D. P. Schaefer, *ibid.*, **10**, 811 (1971).

11) G. R. Brubaker and D. P. Schaefer, *ibid.*, **10**, 968 (1971).

12) G. R. Brubaker and D. P. Schaefer, *ibid.*, **10**, 2170 (1971).

13) B. Bosnich, R. D. Gillard, E. D. McKenzie, and G. A. Webb, *J. Chem. Soc. A*, **1966**, 1331.

14) R. Niththyananthan and M. L. Tobe, *Inorg. Chem.*, **8**, 1589 (1969).

15) L. J. DeHayes, M. Parris, and D. H. Busch, *Chem. Commun.*, **1971**, 1398.

16) S. Yano, K. Furuhashi, and S. Yoshikawa, presented at the 23rd Symposium on Coordination Chemistry, Fukuoka, Japan, October 16—18 (1973).

17) S. Yano, A. Fujioka and S. Yoshikawa, presented at the 24th Symposium on Coordination Chemistry, Kanazawa, Japan, October 7—9 (1974).