none of these species are there any close intermolecular contacts which would suggest packing effects. In the present structure the shortest such distance (Table V) is 3.37 Å.

**Acknowledgment.** We are grateful to Professor Ekk Sinn for assistance during the data collection. This work was supported by National Science Foundation Grant No. CHE 76-04491.

**Registry No.** $\mu$-$C_3H_4$-1,7,2,3-$(C_5H_5)_2Co_2C_2B_3H_3$, 64475-52-1.

**Supplementary Material Available:** Listings of observed and calculated structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

## References and Notes

(1) (a) V. R. Miller and R. N. Grimes, *J. Am. Chem. Soc.*, **95**, 5078 (1973); (b) V. R. Miller and R. N. Grimes, *ibid.*, **98**, 1600 (1976); (c) V. R. Miller, R. Weiss, and R. N. Grimes, *ibid.*, **99**, 5646 (1977).

(2) L. G. Sneddon and D. Voet, *J. Chem. Soc., Chem. Commun.*, 118 (1976).

(3) J. R. Pipal and R. N. Grimes: (a) *Inorg. Chem.*, in press; (b) manuscript in preparation.

(4) (a) K. Wade, *Adv. Inorg. Chem. Radiochem.*, **18**, 1 (1976); (b) R. W. Rudolph, *Acc. Chem. Res.*, **9**, 446 (1976).

(5) We thank Dr. Richard Weiss for supplying the crystal used in this investigation.

(6) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(7) D. T. Cromer and J. T. Waber, "International Tables for X-ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.

(8) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(9) D. T. Cromer and J. A. Ibers, ref 7.

(10) D. P. Freyberg, G. M. Mockler, and E. Sinn, *J. Chem. Soc., Dalton Trans.*, 447 (1976).

(11) (a) D. C. Beer, V. R. Miller, L. G. Sneddon, R. N. Grimes, M. Mathew, and G. J. Palenik, *J. Am. Chem. Soc.*, **95**, 3046 (1973); (b) R. N. Grimes, D. C. Beer, L. G. Sneddon, V. R. Miller, and R. Weiss, *Inorg. Chem.*, **13**, 1138 (1974); (c) V. R. Miller and R. N. Grimes, *J. Am. Chem. Soc.*, **97**, 4213 (1975); (d) R. Weiss and R. N. Grimes, *J. Organomet. Chem.*, **113**, 29 (1976).

(12) W. T. Robinson and R. N. Grimes, *Inorg. Chem.*, **14**, 3056 (1975).

(13) G. E. Herberich, J. Hengesbach, U. Kölle, G. Huttner, and A. Frank, *Angew. Chem., Int. Ed. Engl.*, **15**, 433 (1976).

(14) W. Siebert and K. Kinberger, *Angew. Chem., Int. Ed. Engl.*, **15**, 434 (1976).

(15) W. Siebert, T. Renk, K. Kinberger, M. Bochmann, and C. Krüger, *Angew. Chem., Int. Ed. Engl.*, **15**, 779 (1976).

(16) R. Weiss and R. F. Bryan, *Acta Crystallogr., Sect. B*, **33**, 589 (1977).

(17) R. N. Grimes, W. J. Rademaker, M. L. Denniston, R. F. Bryan, and P. T. Greene, *J. Am. Chem. Soc.*, **94**, 1865 (1972).

(18) J. P. Brennan, R. N. Grimes, R. Schaeffer, and L. G. Sneddon, *Inorg. Chem.*, **12**, 2226 (1973).

(19) F. P. Boer, W. E. Streib, and W. N. Lipscomb, *Inorg. Chem.*, **3**, 1666 (1964).

(20) The chemistry of pentalene and its transition-metal complexes has recently been reviewed: S. A. R. Knox and F. G. A. Stone, *Acc. Chem. Res.*, **7**, 321 (1974).

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# A Cobalt(III) Complex with a Six-Membered Chelate Ring Containing an Axial *C*–Methyl Group. Absolute Configuration and Circular Dichroism of $(-)_{546}$-$\beta$-Oxalato((4*R*,6*R*)-dimethyl-3,7-diazanonane-1,9-diamine)cobalt(III) Perchlorate, $(-)_{546}$-$\beta$-[Co(ox)(*R*,*R*-2,3″,2-tet)]$ClO_4$

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The structure of $(-)_{546}$-$\beta$-[Co(ox)(*R*,*R*-2,3″,2-tet)]$ClO_4$ has been determined from three-dimensional x-ray data collected by the diffractometer method. The compound forms orthorhombic crystals with $a = 9.116$ (1) Å, $b = 25.010$ (1) Å, $c = 7.657$ (2) Å, and $Z = 4$, in space group $P2_12_12_1$. The structure has been solved by the heavy-atom method and refined by least-squares methods with anisotropic temperature factors to give an $R$ value of 0.038 for 1094 observed reflections. The calculated density of 1.654 g/cm$^3$ for four formula units in the unit cell agrees well with the observed density of 1.651 g/cm$^3$. The absolute configuration of the complex is $\Lambda$, the conformations of the two five-membered chelate rings are $\delta$, and the central six-membered chelate ring adopts the chair conformation with one methyl group axial and the other equatorial. The absolute configurations about the two secondary nitrogen atoms are both *S*. The relationship between the absolute configuration around the central metal atom and the circular dichroism in the first absorption band is established.

## Introduction

The stereospecific coordination of optically active tetramines to the octahedral metal complexes has been often observed. It is expected to give important information about the asymmetric synthesis in this system to clarify the factors by which stereoselectivity is induced. Therefore, it is an interesting subject to clarify the stereochemical behavior of the Co(III) complexes of the quadridentate tetramine (4*R*,6*R*)-dimethyl-3,7-diazanonane-1,9-diamine, hereafter *R*,*R*-2,3″,2-tet, which has the six-membered chelate ring with two methyl groups.

In our previous x-ray analysis study of $(+)_{546}$-[Co(ox)(*N*,*N*′-$Me_2$-*R*,*S*-2,3″,2-tet)]$ClO_4$ (I), where *N*,*N*′-$Me_2$-*R*,*S*-2,3″,2-tet is the tetradentate ligand (6*R*,8*S*)-6,8-dimethyl-2,5,9,12-tetraazatridecane, the central six-membered chelate ring adopts the chair conformation with both methyl groups equatorial.[1] On the other hand, Kobayashi et al.[2] reported that each 2,4-pentanediamine chelate ring in the [Co(*R*,*R*-2,4-pentanediamine)$_3$]$^{3+}$ ion took a skew boat conformation with both methyl groups equatorial. Thus, there are two possible conformations for the central 2,4-pentanediamine part of the tetramine in the [Co(ox)(*R*,*R*-2,3″,2-tet)]$^+$ ion known but similar product I oxalate dianion. Consequently, there are four possible isomers in this present complex as shown in Figure 1. Since the $^1$H NMR spectrum of this complex indicated that the two *C*-methyl groups were nonequivalent to each other, the $\Lambda$-cis-$\alpha$ isomer is ruled out.[3] But, it is difficult to assign the geometry of this complex by absorption, CD, and $^1$H NMR spectra. And the relationship between the absolute configuration of the optically active oxalate Co(III) complex with the 2,3,2-tet type ligand and CD spectrum has not been reported except for our previous x-ray study.[1] To elucidate the stereochemistry of this system, the crystal structure of $(-)_{546}$-[Co(ox)(*R*,*R*-2,3″,2-tet)]$ClO_4$ has been determined by x-ray structure analysis.

## Experimental Section

A sample of $(-)_{546}$-$\beta$-[Co(ox)(*R*,*R*-2,3″,2-tet)]$ClO_4$ was generously supplied by Dr. F. Mizukami at the National Chemical Laboratory for Industry.

The specimens are red prismatic crystals elongated along the *b* axis. Weissenberg photographs of (0*kl*) and (*h*0*l*) nets indicated orthorhombic symmetry with the systematic absence of (*h*00) when *h* =

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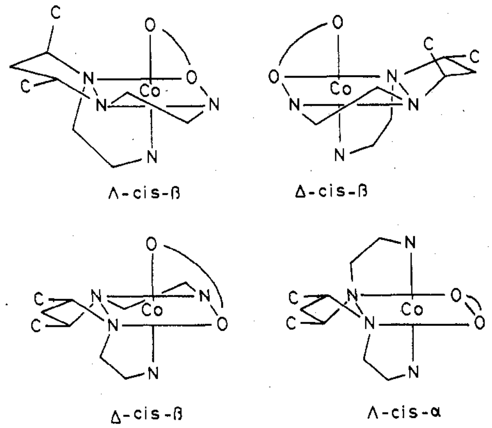

Λ-cis-β

Δ-cis-β

Δ-cis-β

Λ-cis-α

**Figure 1.** Possible isomers.

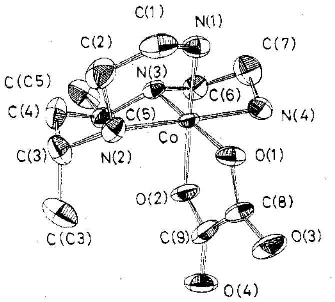

**Figure 2.** A perspective drawing of the complex ion $(-)_{546}$-[Co(ox)(*R*,*R*-2,3″,2-tet)]$^+$ and the numbering scheme for the atoms.

$2n + 1$, $(0k0)$ when $k = 2n + 1$, and $(00l)$ when $l = 2n + 1$. Since the compound is optically active, the space group of the crystal is defined as $P2_12_12_1$. Unit cell parameters were obtained from a least-squares refinement of 13 reflections centered on the four-circle automatic diffractometer, using Mo K$\alpha$ radiation ($\lambda$ 0.7107 Å). The values obtained are $a = 9.116\ (1)$, $b = 25.010\ (1)$, and $c = 7.657(2)$ Å. The density of the crystals, calculated for four formula units per cell, 1.654 g/cm$^3$, is in good agreement with the observed value 1.651 g/cm$^3$, determined by floatation in a mixture of chloroform and dibromoethane.

The crystal used in the data collection was an irregularly shaped thick plate with the approximate dimensions of 0.3 × 0.5 × 0.4 mm. The crystal was mounted with the *c* axis approximately parallel to the instrument axis.

The intensity data were collected by the $2\theta$–$\omega$ scan technique, using Mo K$\alpha$ radiation monochromated by a LiF crystal, on a Rigakudenki four-circle diffractometer. The takeoff angle was 3°. All independent data for the $+h,+k,+l$ quadrant to $(\sin\theta)/\lambda = 0.7035$ $(2\theta = 60°)$ were recorded, with a $2\theta$ scan rate of 2°/min. As a general check on the electronic and crystal stability, the intensities of four standard reflections (401), (004), (062), and (0,12,0) were monitored every 50 reflections. These reflections showed only a 1–2% random variation in intensity, for which no correction was made. Backgrounds were measured for 15 s at both limits of the scan. A total of about 3000 intensities were measured. Reflections for which the intensities were less than three times their standard deviations were regarded as "unobserved" and were not included in subsequent calculations. Thus, 1094 independent reflections were used for the structure determination. The intensities were corrected for Lorentz and polarization factors, but no absorption correction was made since $\mu$ (12.3 cm$^{-1}$) was low. The intensities were reduced to a set of structure factors, *F*.

## Structure Solution and Refinement

A three-dimensional Patterson function revealed the position of the cobalt atom. The remaining nonhydrogen atoms were located by the application of the Fourier method. Several cycles of block-diagonal least-squares refinement using both positional temperature factors reduced the *R* value (defined as $\sum||F_o| - |F_c||/\sum|F_o|$) to 0.155 and a weighted *R* factor ($R' = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$) to 0.176. Further refinement using both positional and anisotropic thermal parameters for nonhydrogen atoms reduced the *R* value to 0.068. At this stage, idealized positional coordinates of the hydrogen atoms except *C*-methyl groups were calculated, assuming a tetrahedral coordination about carbon atoms, with a C–H distance of 1.08 Å. Least-squares refinement, assigning anisotropic thermal parameters to all the atoms except for hydrogen atoms converged with $R = 0.038$ and $R' = 0.039$. A weighting scheme, $w = 1$ if $F_o \geq 10.0$ otherwise $w = 0.5$, was employed. Atomic scattering factors were taken from ref 4. Since the tetramine was prepared from (*R*,*R*)-2,4-pentanediamine, the known absolute configuration of the two asymmetric carbon atoms was used as internal reference asymmetric centers to determine the absolute configuration of the whole complex ion. The effects of anomalous dispersion were included in $F_c$;[5] values of $\Delta f'$ and $\Delta f''$ for Co and Cl were taken from Cromer's tabulation.[6] Final atomic parameters and their estimated standard deviations are listed in Table I. The calculation of the lattice constants, the Fourier synthesis, the least-squares analysis and drawings of the crystal or molecular structures were carried out on a HITAC 8700/8800 computer at the Computer Center of this University, using the RSCL3, ANSFR-2, HBLS-4, and ORTEP2[7] programs of the UNICS system, respectively.

## Description of the Structure

The absolute configuration of the cation has been determined by the known absolute configuration of the two asymmetric carbon atoms of the tetramine ligand as internal reference asymmetric centers. A perspective drawing of the complex ion, together with the atom numbering scheme used, is given in Figure 2, and an arrangement of the unit cell contents is presented in Figure 3. The cation has Λ configuration, and the arrangements of the group around the both secondary nitrogen atoms are *S* configurations. Each conformation of three chelate rings for the tetramine is presentated in Figure 4. The five-membered rings both have the δ-gauche conformation, and the six-membered ring has the chair

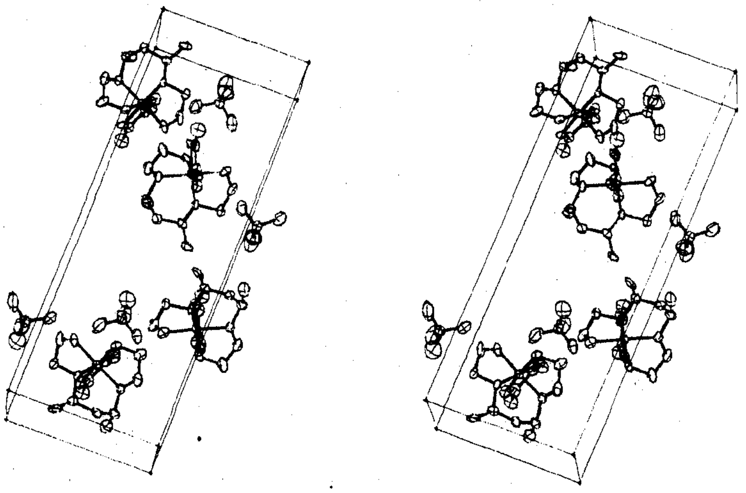

**Figure 3.** A stereoview of the unit cell contents.

**Table I.** Final Atomic Parameters

(a) Final Positional Parameters and Their Estimated Standard Deviations (in Parentheses)[a]

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Co | 603.4 (10) | −1564.4 (3) | 1392.4 (4) |
| N(1) | −145 (6) | −2029 (2) | 3232 (7) |
| N(2) | −1369 (5) | −1226 (2) | 1435 (8) |
| N(3) | 1451 (5) | −1039 (2) | 2980 (6) |
| N(4) | 2516 (6) | −1924 (2) | 1434 (9) |
| O(1) | −95 (5) | −2090 (2) | −259 (5) |
| O(2) | 1226 (5) | −1167 (2) | −565 (5) |
| O(3) | 57 (8) | −2216 (2) | −3144 (6) |
| O(4) | 971 (7) | −1157 (2) | −3459 (6) |
| C(1) | −1768 (9) | −2034 (3) | 3165 (10) |
| C(2) | −2205 (8) | −1460 (4) | 2936 (11) |
| C(3) | −1543 (8) | −610 (3) | 1400 (13) |
| C(4) | −544 (9) | −375 (3) | 2843 (10) |
| C(5) | 1099 (8) | −455 (2) | 2628 (9) |
| C(6) | 3094 (8) | −1114 (3) | 2998 (9) |
| C(7) | 3313 (8) | −1715 (4) | 2968 (12) |
| C(8) | 232 (7) | −1953 (3) | −1878 (7) |
| C(9) | 842 (9) | −1382 (3) | −2009 (8) |
| C(C3) | −1321 (10) | −377 (4) | −381 (13) |
| C(C5) | 1931 (11) | −59 (3) | 3859 (13) |
| Cl | 5533.4 (22) | −1468.8 (4) | 7840.2 (23) |
| O(5) | 5620 (10) | −1071 (3) | 6592 (11) |
| O(6) | 5539 (10) | −1228 (4) | 9518 (10) |
| O(7) | 4193 (7) | −1764 (2) | 7689 (10) |
| O(8) | 6737 (8) | −1829 (3) | 7738 (16) |

(b) Final Thermal Parameters (×$10^4$) and Their Estimated Standard Deviations (in Parentheses)[b]

| | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| Co | 69 (0) | 8 (0) | 36 (0) | 0 (0) | 0 (1) | 0 (0) |
| N(1) | 97 (8) | 10 (1) | 95 (10) | −9 (2) | 3 (6) | 4 (2) |
| N(2) | 65 (6) | 12 (1) | 111 (8) | 0 (2) | 10 (8) | −5 (3) |
| N(3) | 45 (6) | 11 (1) | 73 (7) | −2 (2) | 9 (6) | 0 (2) |
| N(4) | 96 (7) | 16 (1) | 104 (9) | 13 (2) | −20 (9) | 3 (3) |
| O(1) | 114 (6) | 10 (0) | 80 (7) | −9 (1) | −2 (6) | 8 (2) |
| O(2) | 100 (6) | 19 (1) | 46 (6) | 0 (2) | 0 (5) | 0 (2) |
| O(3) | 211 (11) | 22 (1) | 70 (8) | 0 (3) | −15 (7) | −16 (2) |
| O(4) | 195 (10) | 18 (1) | 83 (7) | −1 (2) | 10 (8) | 16 (2) |
| C(1) | 121 (11) | 19 (1) | 108 (14) | −18 (4) | 3 (10) | 8 (3) |
| C(2) | 86 (9) | 21 (2) | 174 (15) | 1 (3) | 42 (10) | 0 (4) |
| C(3) | 109 (10) | 9 (1) | 174 (13) | 5 (2) | −32 (13) | 1 (4) |
| C(4) | 92 (9) | 10 (1) | 193 (14) | 3 (3) | 34 (13) | −9 (3) |
| C(5) | 102 (9) | 9 (1) | 91 (10) | −4 (2) | 16 (8) | 2 (3) |
| C(6) | 67 (8) | 14 (1) | 118 (11) | −3 (2) | −8 (9) | −4 (3) |
| C(7) | 75 (9) | 23 (2) | 198 (17) | 13 (3) | −35 (11) | 6 (5) |
| C(8) | 84 (9) | 13 (1) | 55 (9) | −9 (2) | −7 (6) | −7 (2) |
| C(9) | 105 (10) | 21 (1) | 75 (9) | 2 (3) | 22 (9) | −13 (3) |
| C(C3) | 128 (12) | 18 (2) | 220 (19) | −5 (4) | −38 (14) | 29 (5) |
| C(C5) | 167 (14) | 8 (1) | 216 (19) | −15 (3) | −68 (15) | 4 (4) |
| Cl | 87 (1) | 14 (0) | 138 (2) | 1 (0) | −1 (2) | 0 (0) |
| O(5) | 263 (14) | 31 (2) | 280 (17) | −3 (5) | −3 (18) | 27 (5) |
| O(6) | 196 (12) | 54 (3) | 221 (14) | −3 (5) | −15 (13) | −56 (5) |
| O(7) | 117 (8) | 23 (1) | 307 (15) | −13 (2) | −47 (11) | −12 (4) |
| O(8) | 139 (11) | 33 (2) | 595 (34) | 25 (4) | 67 (17) | 35 (8) |

[a] Values are multiplied by $10^4$. [b] Parameters have the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta hk + 2\beta hl + 2\beta kl)]$.

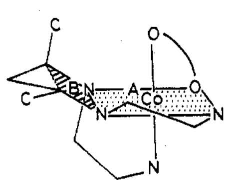

**Figure 4.** The dihedral angle between the plane A and B.

conformation with one methyl group axial and the other equatorial. This is the first time that the chair conformation with an axial methyl group is discovered.

A selection of intramolecular bond distances and bond angles is given in Tables II and III, respectively. The Co–N(2) bond (1.99 (1) Å) is longer than three other Co–N bonds (ca. 1.95 Å). The angle at the cobalt atom, N(2)–Co–O(2) is 93.5 (4)°, which is longer than that in the complex $\Lambda$-(+)$_{546}$-$\beta$-[Co(ox)(*N*,*N*′-Me$_2$-*R*,*S*-2,3″,2-tet)]ClO$_4$ (91.2 (9)°).[1] These are interesting facts considering that the axial *C*-methyl group of the six-membered ring is bonded to the carbon atom adjacent to the N(2) nitrogen atom. The dihedral angle between the plane A and B is 36.4° (Figure 5).

**Table II.** Bond distances (Å) and Their Estimated Standard Deviations (in Parentheses)

| | | | |
|---|---|---|---|
| Co-N(1) | 1.95 (1) | O(3)-C(8) | 1.18 (2) |
| Co-N(2) | 1.99 (1) | O(4)-C(9) | 1.25 (2) |
| Co-N(3) | 1.95 (1) | C(1)-C(2) | 1.50 (2) |
| Co-N(4) | 1.96 (1) | C(3)-C(4) | 1.55 (2) |
| Co-O(1) | 1.93 (1) | C(3)-C(C3) | 1.50 (2) |
| Co-O(2) | 1.89 (1) | C(4)-C(5) | 1.52 (2) |
| N(1)-C(1) | 1.48 (2) | C(5)-C(C5) | 1.56 (2) |
| N(2)-C(2) | 1.50 (2) | C(6)-C(7) | 1.52 (2) |
| N(2)-C(3) | 1.55 (2) | C(8)-C(9) | 1.54 (2) |
| N(3)-C(5) | 1.52 (2) | Cl-O(5) | 1.38 (2) |
| N(3)-C(6) | 1.51 (2) | Cl-O(6) | 1.42 (2) |
| N(4)-C(7) | 1.48 (2) | Cl-O(7) | 1.43 (1) |
| O(1)-C(8) | 1.32 (2) | Cl-O(8) | 1.42 (2) |
| O(2)-C(9) | 1.28 (2) | | |

**Table III.** Bond Angles (deg) and Their Estimated Standard Deviations (in Parentheses)

| | | | |
|---|---|---|---|
| N(1)-Co-N(2) | 85.7 (4) | N(2)-C(3)-C(C3) | 112.9 (10) |
| N(1)-Co-N(3) | 95.2 (4) | C(4)-C(3)-C(C3) | 115.0 (11) |
| N(1)-Co-N(4) | 91.5 (5) | C(3)-C(4)-C(5) | 116.9 (10) |
| N(1)-Co-O(1) | 87.2 (4) | N(3)-C(5)-C(4) | 108.4 (8) |
| N(1)-Co-O(2) | 173.6 (5) | N(3)-C(5)-C(C5) | 113.6 (9) |
| N(2)-Co-N(3) | 93.5 (4) | C(4)-C(5)-C(C5) | 109.2 (10) |
| N(2)-Co-N(4) | 177.2 (5) | N(3)-C(6)-C(7) | 104.6 (9) |
| N(2)-Co-O(1) | 90.1 (4) | N(4)-C(7)-C(6) | 107.4 (10) |
| N(2)-Co-O(2) | 93.5 (4) | O(1)-C(8)-O(3) | 126.4 (9) |
| N(3)-Co-N(4) | 86.9 (4) | O(1)-C(8)-C(9) | 112.7 (9) |
| N(3)-Co-O(1) | 175.8 (4) | O(3)-C(8)-C(9) | 120.9 (10) |
| N(3)-Co-O(2) | 91.3 (4) | O(2)-C(9)-O(4) | 123.5 (9) |
| N(4)-Co-O(1) | 89.5 (4) | O(2)-C(9)-C(8) | 115.7 (9) |
| N(4)-Co-O(2) | 89.3 (5) | O(4)-C(9)-C(8) | 120.8 (10) |
| O(1)-Co-O(2) | 86.4 (4) | O(5)-Cl-O(6) | 108.7 (11) |
| C(2)-N(2)-C(3) | 110.5 (10) | O(5)-Cl-O(7) | 111.3 (10) |
| C(5)-N(3)-C(6) | 109.2 (8) | O(5)-Cl-O(8) | 112.0 (11) |
| N(1)-C(1)-C(2) | 105.1 (9) | O(6)-Cl-O(7) | 107.2 (10) |
| N(2)-C(2)-C(1) | 109.2 (10) | O(6)-Cl-O(8) | 108.4 (11) |
| N(2)-C(3)-C(4) | 107.8 (9) | O(7)-Cl-O(8) | 109.1 (9) |

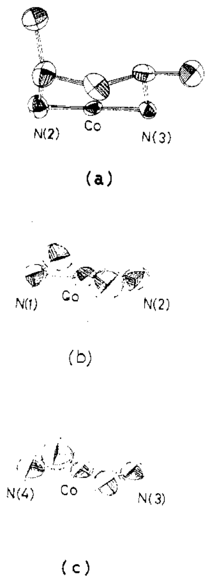

**Figure 5.** A perspective drawing of the chelate rings: (a) central six-membered ring, (b) out-of-plane five-membered ring, (c) in-plane five-membered ring.

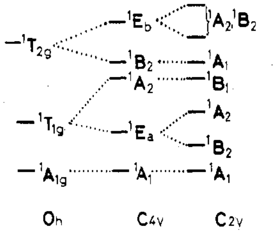

**Figure 6.** Energy levels for tetragonal and dihedral complexes of low-spin Co(III).

Comparing with the corresponding value of 40.6° in the $[Co(ox)(N,N'\text{-}Me_2\text{-}R,S\text{-}2,3'',2\text{-tet})]^+$ ion, this is considerably flattened. The elongation of the bond length and the ring flattening mentioned above may be attributed to the interaction between the axial methyl group and the O atom of the axial ligand on the metal ion. Changes in the geometry of the chelate ring skelton caused by such interactions are also indicated by conformational studies of metal chelates.[8]

The ring angles at the cobalt atom for the five-membered diamine chelate rings are 85.7 (4) and 86.9 (4)° for N(1)–Co–N(2) and N(3)–Co–N(4), respectively, which are normal for Co(III) five-membered diamine chelate rings. The angle at the cobalt for the six-membered ring N(2)–Co–N(3) is 93.5 (4)°, which is similar to that for the $(+)_{546}$-$[Co(ox)(N,N'\text{-}Me_2\text{-}R,S\text{-}2,3'',2\text{-tet})]^+$ ion,[1] 92.8°, but significantly larger than that in the complex $(+)_{470}$-β-*cis*-$[Co(NO_2)_2(5\text{-methyl-}1,4,8,11\text{-tetraazaundecane})]^+$,[9] 89.9°.

## Discussion

This complex[3] was prepared from the *trans*-$[CoCl_2(R,R\text{-}2,3'',2\text{-tet})]^+$ by the action of sodium oxalate. On the basis of the absorption, circular dichroism, and proton magnetic resonance spectra, the complex was assigned to be *trans*-*S*,*S*-$[CoCl_2(R,R\text{-}2,3'',2\text{-tet})\delta\lambda\delta)^+$, where *S*,*S* refers to the configuration of the coordinated secondary nitrogen atoms and δλδ describes the chelate ring conformation (δ = a five-membered gauche conformation, λ = a six-membered λ skew boat conformation). The absolute configurations of the secondary nitrogen atoms of our present oxalato complex are also *S*,*S*. This indicates that this reaction from trans dichloro to oxalato complex proceeds with the retention of the configuration around the secondary nitrogen atoms of the tetramine (see ref 3). This fact would provide fundamental information to make clear the reaction mechanism from the trans dichloro complex to the oxalato complex.

There are four possible isomers in this system as shown in Figure 1. The Λ-cis β isomer was found to be produced from the $[Co(ox)_3]^{3-}$ ion and the tetramine, which suggests that the Λ-cis β isomer is the most preferred form in these oxalato complexes. In either preparation method, the isomer which has the skew boat six-membered ring in the tetramine was not produced. Consequently, the six-membered ring prefers the chair conformation to the skew boat conformation even if one *C*-methyl group takes axial orientation.

**Absolute Configuration and Circular Dichroism.** It has been often assumed that *cis*-$[CoN_4O_2]^+$ such as oxalatotetraaminecobalt(III) complex ions were approximated to $C_2$ symmetry. In complexes of $C_2$ symmetry, the $^1T_{1g}(O_h)$ state is split into one component with A symmetry and two components with B symmetry as shown in Figure 6. It is well known that the CD sign of the $^1A_1 \rightarrow {}^1A_2(E_a)$ transition (the dominant band) correlates closely to absolute configurations for a series of complexes of $C_2$ symmetry. This correlation should be confirmed on the basis of x-ray structure analysis. We have even clarified absolute configurations for $(+)_{546}$-β-$[Co(ox)(N,N'\text{-}Me_2\text{-}R,S\text{-}2,3'',2\text{-tet})]^+$ and $(-)_{546}$-β-$[Co(ox)(R,R\text{-}2,3'',2\text{-tet})]^+$. The CD curve of $(-)_{546}$-Λ-β-$[Co(ox)(R,R\text{-}2,3'',2\text{-tet})]ClO_4$ is very similar to that of the complex $(-)_{546}$-$[Co(ox)(N,N'\text{-}Me_2\text{-}R,S\text{-}2,3'',2\text{-tet})]ClO_4$ which is an enantiomer of $(+)_{546}$-$[Co(ox)(N,N'\text{-}Me_2\text{-}R,S\text{-}2,3'',2\text{-tet})]ClO_4$ determined to have the Δ-β configuration (Figure 7). These results lead to the conclusion that when the oxalatocobalt(III) complexes of 3,7-diaza-1,9-nonanediamine (2,3,2-tet) and its derivatives give two circular dichroism bands with opposite signs in the first absorption region, an enantiomer, which has a lower energy positive Cotton effect and a higher energy negative one, should be assigned the Λ configuration.

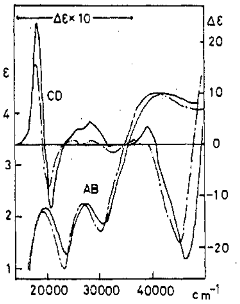

**Figure 7.** CD spectra of (—) $(-)_{546}$-Λ-β-$[Co(ox)(R,R\text{-}2,3'',2\text{-tet})]^+$ and (----) $(-)_{546}$-Λ-β-$[Co(ox)(N,N'\text{-}Me_2\text{-}R,S\text{-}2,3'',2\text{-tet})]^+$.

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**Registry No.** $(-)_{546}$-Λ-β-$[Co(ox)(R,R\text{-}2,3'',2\text{-tet})]ClO_4$, 55683-82-4.

**Supplementary Material Available:** A listing of structure factor amplitudes (4 pages). Ordering information is given on any current masthead page.

## References and Notes

(1) S. Yano, K. Furuhashi, and S. Yoshikawa, *Bull. Chem. Soc. Jpn.*, **50**, 685 (1977).
(2) A. Kobayashi, F. Marumo, and Y. Saito, *Inorg. Nucl. Chem. Lett.*, **7**, 777 (1971).
(3) F. Mizukami, *Bull. Chem. Soc. Jpn.*, **48**, 472 (1975).
(4) "International Tables for X-ray Crystallography", Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 270 and 276.
(5) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, **17**, 781 (1964).
(6) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
(7) C. K. Johnson "ORTEP", Report No. ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.
(8) J. R. Gollogly and C. J. Hawkins, *Inorg. Chem.*, **11**, 156 (1972).
(9) P. W. R. Corfield, J. C. Dabrowiak, and E. S. Gore, *Inorg. Chem.*, **12**, 1734 (1973).