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Absolute Configuration and Circular Dichroism of $(+)_{546}$-β-(Oxalato)((2*S*,4*S*,9*S*,11*S*)-4,9-dimethyl-5,8-diazadodecane-2,11-diamine)cobalt(III) Bromide Trihydrate, $(+)_{546}$-β-[Co(ox)(*S*,*S*,*S*,*S*-3″,2,3″-tet)]Br·3H_2O

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The crystal and molecular structure of $(+)_{546}$-β-(oxalato)((2*S*,4*S*,9*S*,11*S*)-4,9-dimethyl-5,8-diazadodecane-2,11-diamine)cobalt(III) bromide trihydrate ($(+)_{546}$-β-[Co(ox)(*S*,*S*,*S*,*S*-3″,2,3″-tet)]Br·3H_2O) has been determined from three-dimensional X-ray counter data. The complex crystallizes in the monoclinic system, space group $P2_1$, with $a = 10.332$ (1) Å, $b = 13.170$ (1) Å, $c = 8.404$ (1) Å, and $\beta = 107.85$ (1)°. With $Z = 2$, the observed and calculated densities are 1.550 and 1.557 g cm^{-3}, respectively. The structure was refined by least-squares methods to a final value of $R = 0.063$ for 2016 independent reflections with $F_o > 3\sigma(F_o)$. The absolute configuration of the complex cation is Λ, the conformations of the two six-membered chelate rings are the chair conformation with one methyl group axial and the other equatorial, and the central five-membered chelate ring adopts λ-gauche conformation. The absolute configurations about the two secondary nitrogen atoms are both *R*. The relationship between the absolute configuration around the central metal atom and the circular dichroism in the first absorption band is confirmed.

Introduction

X-ray crystal structure investigations of transition-metal–polyamine chelates have played an important role in elucidating the relationship between the structure and observed properties of these compounds. In a series of these studies, we have determined the crystal and molecular structure of some optically active cobalt(III) complexes which have a six-membered chelate ring.[1,2] In Δ-β-[Co(ox)(*N*,*N*′-Me$_2$-*R*,*S*-2,3″,2-tet)]ClO$_4$,[1] 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, and Λ-β-[Co(ox)(*R*,*R*-2,3″,2-tet)]ClO$_4$,[2] where *R*,*R*-2,3″,2-tet is the tetradentate ligand (4*R*,6*R*)-dimethyl-3,7-diazanonane-1,9-diamine, each central six-membered 2,4-pentanediamine part adopts the chair conformation. In the latter case, the six-membered chelate ring takes the chair conformation with one methyl group axial and the other equatorial.

When (*S*,*S*)-2,4-pentanediamine is coordinated to a metal as a bidentate ligand, there are two possible conformations. The chair conformation of the ring has one methyl group axial and the other equatorial; but in the δ-skew boat conformation both methyl groups are equatorially disposed. From recent crystal structure analysis studies both conformations have been observed.[3,4] Thus, there are two possible conformations for the 2,4-pentanediamine parts in the [Co(L)(*S*,*S*,*S*,*S*-3″,2,3″-tet)]$^+$ ion, where L represents a bidentate ligand. And the relationship between the absolute configuration of the optically active (oxalato)cobalt(III) complex with 3,2,3-tet (4,7-diazadecane-1,10-diamine) and its C-methylated derivatives and the circular dichroism in the first absorption band has not been confirmed by X-ray structural study. To elucidate the stereochemistry of this system, we undertook a crystal and molecular structure determination of $(+)_{546}$-[Co(ox)(*S*,*S*,*S*,*S*-3″,2,3″-tet)]Br·3H_2O.[5]

Experimental Section

The instruments used in obtaining the physical measurements were the following: visible and ultraviolet spectra, a Shimazu MPS-50L spectrometer; circular dichroism spectra, a Jasco J-20 spectropolarimeter.

A. Preparation of *S*,*S*,*S*,*S*-3″,2,3″-tet. This active tetraamine ligand was prepared by a method similar to that described for *R*,*R*,*R*,*R*-3″,2,3″-tet[6,7] by using *S*,*S*-2,4-ptdn in place of *R*,*R*-2,4-ptdn (ptdn = pentanediamine).

B. Preparation of $(+)_{546}$-β-[Co(ox)(*S*,*S*,*S*,*S*-3″,2,3″-tet)]Br·3H_2O. A solution containing *trans*-[CoCl$_2$(*S*,*S*,*S*,*S*-3″,,2,3″-tet)]ClO$_4$·3H_2O[6] (5 g) and 2.4 g of potassium oxalate hydrate in 100 mL of water was warmed on a steam bath for 4 h at 70 °C. After being filtered and cooled to room temperature, the solution was passed through a Dowex 1-X8 (100–200 mesh) anion-exchange resin in the Br form (40–50-fold excess) and evaporated to 30 mL. The reddish violet crystals which formed on cooling of the solution were filtered, washed with ethanol and ether, and dried under vacuum. Recrystallization of the solid from the minimum volume of hot water at 70 °C gave well-developed reddish violet crystals. Anal. Calcd for [CoC$_{14}$H$_{30}$N$_4$O$_4$]Br·3H_2O: C, 32.95; H, 7.11; N, 10.98. Found: C, 33.36; H, 6.68; N, 11.23.

Crystal Data. Weissenberg photographs indicated a monoclinic unit cell with systematic extensions for 0*k*0, $k = 2n + 1$. Of the two possible space groups $P2_1$ and $P2_1m$, the latter was eliminated because of the optical activity of the compound. The unit cell dimensions were obtained by least-squares refinement of 12 high-angle reflections centered on a Rigakudenki four-circle automated diffractometer using Mo Kα radiation (λ 0.7107 Å) and are $a = 10.332$ (1) Å, $b = 13.170$ (1) Å, $c = 8.404$ (1) Å, and $\beta = 107.85$ (1)°. With $Z = 2$ and the molecular weight of this complex, the calculated density is 1.557 g cm^{-3} compared with a measured density of 1.550 g cm^{-3} obtained by flotation in a dibromoethane–carbon tetrachloride mixture.

Intensity Data Collection. The crystal used in the data collection was an irregularly shaped thick plate with the approximate dimensions 0.4 × 0.5 × 0.3 mm. The crystal was mounted with the *b* axis approximately parallel to the instrument axis. Diffraction data were collected on a Rigakudenki four-circle automated diffractometer. The 2θ–ω-scan method was employed with a scanning rate of 2°/min. Stationary-crystal, stationary-counter background counts of 30 s were taken on each side of the reflection. All possible reflections with indices hkl and $\bar{h}kl$ with 2θ values between 5 and 60° were collected by using Mo Kα radiation monochromated by a LiF crystal. The takeoff angle was 3°. Four standard reflections were monitored every 50 reflections and exhibited no systematic decrease in intensity. A total of about 2500 reflections were measured and the standard Lorentz and polarization corrections applied. Of the 2500 reflections collected, 2016 had $F_o > 3\sigma(F_o)$ and were considered observed. Absorption correction ($\mu = 28.03$ cm^{-1}) was applied. For determination of the absolute configuration of the complex ion, some reflections with indices hkl and $\bar{h}\bar{k}\bar{l}$ were collected by using Cu Kα (λ 1.542 Å) radiation on the diffractometer.

Solution and Refinement of the Structure. A three-dimensional Patterson map was calculated, and the positions of the Co and Br atoms were determined. The bromo *y* coordinate was arbitarily assigned as 0.25 because $P2_1$ does not have a unique origin on the *b* axis. Careful peak selection coupled with bond-length calculations allowed the remaining nonhydrogen atoms except for water oxygen atoms to be located. Several cycles of block-diagonal least-squares refinement with isotropic temperature factors reduced R and R' to 0.150 and 0.186, respectively, where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R' = [\sum w(F_o - |F_c|)^2/\sum wF_o^2]^{1/2}$. A difference electron density map calculated at this point revealed the positions of three oxygen atoms.

The absolute configuration of the complex was determined by using the absorption-edge technique.[8] Some reflections with indices hkl and $\bar{h}\bar{k}\bar{l}$ were collected with Cu Kα radiation. The inequality re-

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Table I. Determination of the Absolute Configuration: Relations between *F*(*hkl*) and *F*($\bar{h}\bar{k}\bar{l}$) Observed and Calculated for the Λ Configuration

h	*k*	*l*	F_o-(*hkl*)		F_o-($\bar{h}\bar{k}\bar{l}$)	F_c-(*hkl*)		F_c-($\bar{h}\bar{k}\bar{l}$)
2	1	1	36	<	49	36	<	48
2	2	1	66	<	72	65	<	69
3	2	2	33	>	28	31	>	26
4	2	2	23	>	19	22	>	20
2	2	3	35	<	41	34	<	38
1	4	4	16	>	9	13	>	5
2	2	4	18	<	24	17	<	22
2	3	4	16	>	7	15	>	9
2	4	4	11	>	4	13	>	5
3	1	4	55	>	51	56	>	51
3	3	4	12	>	5	13	>	6
4	3	4	13	>	6	15	>	8

lationships which were observed for some Bijvoet pairs of *hkl* and $\bar{h}\bar{k}\bar{l}$ are shown in Table I. Accordance between the observed and calculated differences indicates that the complex cation has the Λ absolute configuration, in agreement with the known absolute configuration of the (*S*,*S*)-2,4-pentanediamine[3] used in the synthesis of the tetraamine.

The effects of anomalous dispersion were included in F_c;[9] values of $\Delta f'$ and $\Delta f''$ for Co and Br were taken from Cromer's tabulation.[10] A weighting scheme

$$w = (F_m/F_o)^2 \quad \text{if } F_o > F_m\ (=40.0)$$

$$w = 1.0 \quad \text{if } F_o \le F_m\ (=40.0)$$

was employed. Atomic scattering factors were taken from ref 11. Least-squares refinement, on assignment of anisotropic thermal parameters to all the atoms except for hydrogen atoms, converged with $R = 0.066$ and $R' = 0.085$.

The final structure has the Λ configuration. When the coordinates were inverted so as to give the Δ structure, convergence was reached with $R = 0.068$ and $R' = 0.088$, values which are significantly higher than the corresponding values 0.066 and 0.085 for the Λ structure. This result agreed with the earlier determination by using the absorption-edge technique.

At this stage, idealized locations of the hydrogen atoms except *C*-methyl groups were calculated by assuming a tetrahedral coordination about carbon atoms and nitrogen atoms, with a C–H distance of 1.08 Å and a N–H distance of 1.03 Å. On inclusion of fixed contributions from 18 hydrogen atoms with an isotropic thermal parameter $B = 3.0$ Å^2, further refinement of the nonhydrogen parameters converged with $R = 0.063$ and $R' = 0.820$. A final difference Fourier map still showed peaks at height up to 2 e/Å^3 around the bromine and cobalt atoms, although the electron density did not rise above 2 e/Å^3 elsewhere. The final positional and thermal parameters along with their standard deviations are listed in Table II. A compilation of observed and calculated structure factors is available.[12] All calculations were performed on a HITAC 8700/8800 computer at the Computer Center of this University. Programs used were RSCL3 (lattice constants), INCOR3 (absorption correction), ANSFR-2 (Fourier synthesis), BLAN-2 (least-squares refinement), COSMO (distances, angles, and their esd's), and ORTEP2 (thermal ellipsoid plotting program).[13]

Results and Discussion

Description and Discussion of the Structure. The AB and CD spectra are shown in Figure 1, and they are summarized in Table III. The pattern of the first absorption band indicates that the present complex has two coordinated oxygen atoms in the cis positions. The complex shows a large positive Cotton effect in the first absorption region. This implies that the complex can be assigned to the Λ absolute configuration. The geometry of the complex cation is confirmed by the present structure analysis study (Figure 2). The tetraamine ligand, NH$_2$CH(CH$_3$)CH$_2$CH(CH$_3$)NHCH$_2$CH$_2$NHCH(CH$_3$)CH$_2$CH(CH$_3$)NH$_2$, is coordinated to the cobalt atom in the Λ-cis-β geometry. The cobalt atom is situated at the center of a slightly distorted octahedron. The absolute configuration of the complex, determined by the Bijvoet method,[8] is Λ in agreement with the assignment made by analysis of the circular dichroism spectrum of the complex.

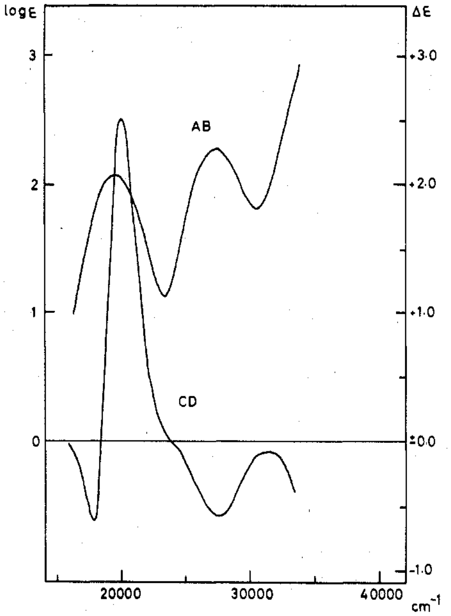

Figure 1. AB and CD spectra of the $(+)_{546}$-β-[Co(ox)(*S*,*S*,*S*,*S*-3″,2,3″)]Br·3H$_2$O in water.

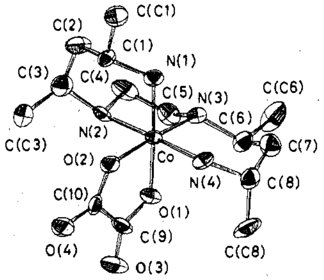

Figure 2. Perspective drawing of the complex ion $(+)_{546}$-Λ-β-[Co(ox)(*S*,*S*,*S*,*S*-3″,2,3″-tet)]$^+$ and the numbering scheme for the atoms.

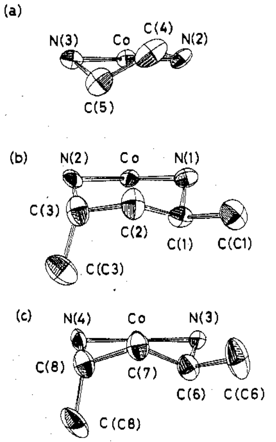

Figure 3. Perspective drawing of the chelate rings: (a) central five-membered ring; (b) out-of-plane six-membered ring; (c) in-plane five-membered ring.

A detailed view of the complex cation is given in Figure 2, and the intramolecular distances and bond angles are given in Tables IV and V. The arrangement of the group around the secondary nitrogen atoms is an *R* configuration in the notation of Cohen, Ingold, and Prelog.[14] Each conformation of three chelate rings for the tetraamine is presented in Figure 3. The six-membered rings both have the chair conformation with one methyl group axial and the other equatorial, and the

Table II. Final Atomic Parameters

(a) Final Positional Parameters[a,c]

atom	x	y	z
Co	72 (1)	1021 (1)	2832 (1)
N(1)	−1123 (6)	2078 (6)	1514 (8)
N(2)	−847 (7)	−23 (5)	1143 (9)
N(3)	1422 (6)	1117 (5)	1610 (8)
N(4)	945 (7)	2056 (6)	4540 (8)
O(1)	1143 (6)	−22 (4)	4178 (8)
O(2)	−1126 (5)	777 (5)	4117 (7)
O(3)	1166 (8)	−1131 (7)	6183 (10)
O(4)	−1448 (7)	−404 (7)	5905 (9)
C(1)	−2629 (7)	1848 (7)	859 (11)
C(2)	−2903 (10)	1014 (8)	−369 (12)
C(3)	−2347 (11)	−33 (8)	306 (13)
C(4)	−103 (14)	−62 (9)	−141 (13)
C(5)	1338 (11)	134 (8)	699 (13)
C(6)	2876 (9)	1378 (8)	2581 (12)
C(7)	2947 (10)	2351 (8)	3566 (13)
C(8)	2433 (9)	2273 (8)	5103 (12)
C(C1)	−3359 (10)	2834 (9)	99 (16)
C(C3)	−3141 (11)	−531 (10)	1370 (17)
C(C6)	3725 (10)	1502 (14)	1378 (15)
C(C8)	3192 (11)	1545 (12)	6402 (12)
C(9)	651 (10)	−452 (8)	5218 (11)
C(10)	−777 (9)	−7 (9)	5101 (11)
Br	86.4 (10)	2500.0 (0)	8091.3 (10)
O(5)	5777 (15)	78 (20)	5349 (27)
O(6)	6621 (12)	2113 (18)	5382 (27)
O(7)	6107 (22)	3867 (23)	4489 (89)

(b) Final Thermal Parameters[a-c]

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	52.9 (8)	27.7 (5)	43.1 (11)	1.9 (7)	20.1 (8)	1.8 (7)
N(1)	64 (7)	43 (4)	55 (9)	1 (4)	24 (7)	0 (5)
N(2)	82 (7)	25 (3)	66 (10)	−4 (4)	38 (7)	12 (5)
N(3)	59 (6)	28 (3)	63 (8)	8 (4)	16 (6)	−5 (5)
N(4)	66 (7)	46 (4)	46 (9)	4 (4)	11 (7)	−13 (5)
O(1)	89 (7)	27 (3)	78 (9)	6 (4)	28 (6)	12 (4)
O(2)	58 (5)	60 (4)	64 (8)	−5 (4)	20 (5)	8 (5)
O(3)	139 (10)	79 (6)	119 (12)	2 (7)	31 (9)	56 (8)
O(4)	96 (8)	88 (6)	91 (10)	−16 (6)	34 (8)	28 (7)
C(1)	33 (6)	44 (5)	94 (13)	4 (5)	5 (8)	12 (7)
C(2)	122 (11)	42 (5)	85 (12)	9 (8)	3 (10)	5 (8)
C(3)	113 (12)	37 (5)	99 (15)	−7 (6)	8 (12)	−11 (7)
C(4)	181 (16)	38 (5)	60 (13)	−3 (7)	68 (12)	−11 (7)
C(5)	106 (12)	51 (6)	109 (15)	0 (7)	67 (12)	0 (8)
C(6)	52 (8)	61 (6)	91 (13)	−2 (5)	26 (8)	−4 (8)
C(7)	89 (10)	54 (7)	117 (15)	−8 (6)	50 (10)	−4 (8)
C(8)	82 (9)	48 (6)	87 (13)	−17 (6)	21 (9)	−18 (7)
C(C1)	79 (11)	52 (6)	180 (20)	11 (7)	10 (12)	28 (10)
C(C3)	85 (11)	68 (8)	168 (21)	−24 (8)	3 (13)	21 (12)
C(C6)	70 (10)	152 (15)	125 (18)	−22 (10)	51 (12)	−39 (14)
C(C8)	81 (11)	113 (11)	66 (13)	0 (9)	−13 (10)	2 (11)
C(9)	117 (11)	35 (4)	70 (12)	−10 (7)	37 (10)	16 (7)
C(10)	59 (9)	67 (6)	61 (11)	−38 (6)	11 (8)	−10 (7)
Br	139.2 (12)	37.8 (4)	85.8 (10)	−0.8 (7)	62.0 (10)	7.0 (7)
O(5)	182 (19)	307 (30)	420 (45)	73 (19)	106 (25)	−37 (32)
O(6)	147 (15)	282 (27)	502 (50)	29 (18)	58 (23)	159 (35)
O(7)	301 (34)	208 (26)	3244 (385)	19 (32)	647 (104)	34 (110)

[a] Values are multiplied by 10^4. [b] Parameters have the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [c] Estimated standard deviations in parentheses.

Table III. Electronic Absorption (AB) and Circular Dichroism (CD) Data of $(+)_{546}$-Λ-β-[Co(ox)(*S,S,S,S*-3'',2,3''-tet)]Br·3H_2O: $\tilde{\nu}$ in 10^3 cm^{-1}

AB $\tilde{\nu}$ (max log ϵ)	CD $\tilde{\nu}$ (max $\epsilon_l - \epsilon_r$)
19.23 (2.07)	17.76 (−0.623)
	20.00 (+2.517)
27.24 (2.27)	27.77 (−0.590)

central five-membered ring adopts the λ-gauche conformation.[15] An axial methyl group on the in-plane six-membered chelate ring exists adjacently to the terminal nitrogen atom (N(4)). The other on the out-of-plane six-membered chelate ring is lying near the secondary nitrogen atom (N(2)). The Co–N(1) bond length is 1.96 (1) Å. This distance is significantly shorter than the values of 1.99 (1), 1.97 (1), and 2.00 (1) Å for the chelate bonds Co–N(4), Co–N(3), and Co–N(2), respectively. The ring angle at the cobalt atom for the five-membered diamine part, N(2)–Co–N(3), is 86.1 (5)°, which is normal for Co(III) five-membered diamine chelate rings. In the trans 3,2,3-tet complex,[16] the corresponding angle is 85.6°. This particular parameter of the five-membered chelate ring is relatively insensitive to the presence of fused

Table IV. Bond Distances (Å)[a]

Co–N(1)	1.963 (15)	O(2)–C(10)	1.303 (19)
Co–N(2)	1.996 (11)	O(3)–C(9)	1.215 (21)
Co–N(3)	1.973 (10)	O(4)–C(10)	1.224 (21)
Co–N(4)	1.985 (12)	C(1)–C(2)	1.475 (22)
Co–O(1)	1.905 (10)	C(1)–C(C1)	1.538 (24)
Co–O(2)	1.904 (10)	C(2)–C(3)	1.535 (24)
N(1)–C(1)	1.514 (18)	C(3)–C(C3)	1.533 (27)
N(2)–C(3)	1.493 (21)	C(4)–C(5)	1.463 (26)
N(2)–C(4)	1.506 (23)	C(6)–C(7)	1.516 (23)
N(3)–C(5)	1.492 (20)	C(6)–C(C6)	1.537 (28)
N(3)–C(6)	1.514 (19)	C(7)–C(8)	1.543 (23)
N(4)–C(8)	1.491 (20)	C(8)–C(8)	1.484 (26)
O(1)–C(9)	1.270 (19)	C(9)–C(10)	1.564 (23)

[a] Estimated standard deviations in parentheses.

Table V. Bond Angles (deg)[a]

N(1)–Co–N(2)	90.4 (5)	C(1)–C(2)–C(3)	116.2 (12)
N(1)–Co–N(3)	94.8 (5)	N(2)–C(3)–C(2)	112.5 (11)
N(1)–Co–N(4)	89.4 (5)	N(2)–C(3)–C(C3)	113.1 (12)
N(1)–Co–O(1)	176.2 (6)	C(2)–C(3)–C(C3)	113.3 (13)
N(1)–Co–O(2)	91.9 (5)	N(2)–C(4)–C(5)	108.4 (11)
N(2)–Co–N(3)	86.1 (5)	N(3)–C(5)–C(4)	107.0 (11)
N(2)–Co–N(4)	178.4 (6)	N(3)–C(6)–C(7)	111.1 (10)
N(2)–Co–O(1)	89.3 (5)	N(3)–C(6)–C(C6)	110.0 (12)
N(2)–Co–O(2)	92.1 (5)	C(7)–C(6)–C(C6)	109.1 (13)
N(3)–Co–N(4)	95.5 (5)	C(6)–C(7)–C(8)	115.4 (12)
N(3)–Co–O(1)	88.9 (4)	C(4)–C(8)–C(7)	109.4 (10)
N(3)–Co–O(2)	173.0 (5)	N(4)–C(8)–C(C8)	111.7 (11)
N(4)–Co–O(1)	90.8 (5)	C(7)–C(8)–C(C8)	114.8 (13)
N(4)–Co–O(2)	86.3 (5)	O(1)–C(9)–O(3)	127.0 (12)
O(1)–Co–O(2)	84.3 (4)	O(1)–C(9)–C(10)	111.0 (11)
C(3)–N(2)–C(4)	110.3 (12)	O(3)–C(9)–C(10)	122.0 (13)
C(5)–N(3)–C(6)	111.5 (11)	O(2)–C(10)–O(4)	126.6 (11)
N(1)–C(1)–C(2)	111.0 (10)	O(2)–C(10)–C(9)	114.2 (11)
N(1)–C(1)–C(C1)	107.5 (10)	O(4)–C(10)–C(9)	119.3 (12)
C(2)–C(1)–C(C1)	112.0 (12)		

[a] Estimated standard deviations in parentheses.

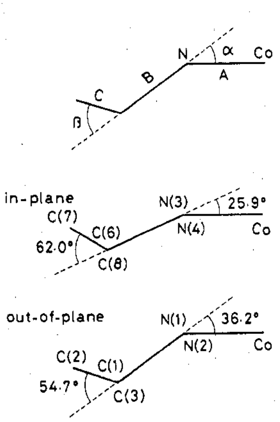

Figure 4. Dihedral angles between the planes A and B and between the planes B and C.

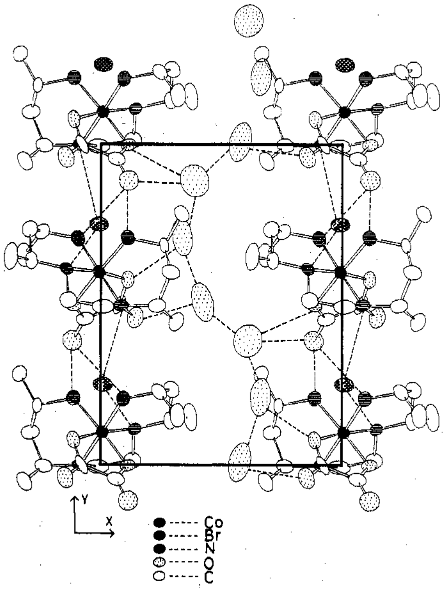

Figure 5. Crystal structure viewed down the *c* axis. Broken lines indicate the hydrogen bonds.

Table VI. H-Bonding Angles and Interatomic Distances <3.5 Å outside the Complex Ions: A–H···B

A	B	A···B, Å	AHB, deg	symmetry of atom B
N(2)	Br	3.37 (1)	152.5	$-x, y, 1-z$
N(3)	Br	3.39 (1)	161.7	$x, y, -1+z$
N(1)	O(3)	3.06 (1)	167.2	$-x, -1+y, 1-z$
N(4)	O(3)	3.16 (1)	151.4	$-x, -1+y, 1-z$
O(1)	O(7)	3.08 (7)		$1-x, y, 1-z$
O(2)	O(6)	3.34 (4)		$-1+x, y, z$
O(3)	O(7)	3.04 (7)		$1-x, y, 1-z$
O(5)	O(6)	2.82 (4)		x, y, z
O(5)	O(7)	2.55 (8)		$1-x, y, 1-z$
O(6)	O(7)	2.44 (8)		x, y, z

rings. The ring angles at the cobalt atom for the six-membered rings are 95.5 (5) and 90.4 (5)°, for N(3)–Co–N(4) and N(1)–Co–N(2), respectively. The value of the former is significantly large as compared with the reported values in the $(+)_{546}$-Δ-β-[Co(ox)(*N*,*N′*-Me_2-*R*,*S*-2,3″,2-tet)]$^+$ ion, 91.7 (9)°,[1] in the $(-)_{546}$-Λ-β-[Co(ox)(*R*,*R*-2,3″,2-tet)]$^+$ ion, 93.5 (4)°,[2] and in the $(+)_{470}$-Δ-β-[Co$(NO_2)_2$((4*S*)-4-methyl-3,7-diazanonane-1,9-diamine)]$^+$ ion, 89.9 (2)°.[17] In the 3,2,3-tet complex the angles are 92.5 (3) and 92.6 (3)°,[16] while in the complex *trans*-[CoCl_2(tn)$_2$]Cl·HCl·$2H_2O$[18] and [Co(tn)$_3$]Br_3·H_2O,[19] where tn represents the simple bidentate ligand trimethylenediamine, the angles are 95.4 and 94.5°, respectively. Clearly the N(1)–Co–N(2) chelate ring of the tetraamine in the present complex is fairly strain relieving.

With the exception of C(2)–C(3) and C(7)–C(8), the average C–C distance of the ring carbon atoms is 1.49 (2) Å. The bond distances C(2)–C(3) and C(7)–C(8) are 1.54 (2) and 1.54 (2) Å, respectively, which are significantly longer than the other C–C bonds. Since C(3) and C(8) have an axial *C*-methyl group, the elongation of the bond distances mentioned above may be attributed to the interaction between the axial methyl groups and the adjacent chelate rings.

The conformations of the six-membered chelate rings in the tetraamine are represented diagrammatically in Figure 4. We discuss the conformations of six-membered chelate rings in terms of dihedral angles α and β, where α is the dihedral angle between the planes A and B and β is that between the planes B and C (Figure 4). The values of α and β are 25.9, 62.0° and 36.2, 54.7° for the in-plane and out-of-plane chelate rings, respectively. The values of α in the Δ-β-[Co(ox)(*N*,*N′*-Me_2-*R*,*S*-2,3″,2-tet)]$^+$ ion, the Λ-β-[Co(ox)(*R*,*R*-2,3″,2-tet)]$^+$ ion, and the Δ-β-[Co$(NO_2)_2$(*S*-2,3′,2-tet)]$^+$ ion, where *S*-2,3′,2-tet is the tetradentate ligand (4*S*)-4-methyl-3,7-diazanonane-1,9-diamine, are 40.6, 36.4, and 41.2°, respectively. The value of β is 54.8° in the last complex ion. Clearly, the magnitude of the ring flattening of the complexes containing an axial *C*-methyl group(s) is larger than that of the complexes having the equatorial methyl groups only. The ring flattening mentioned above is presumably due to the interaction between the axial methyl group(s) and the neighboring atoms. This puckering is in response to the large bond angles of C(1)–C(2)–C(3) and C(6)–C(7)–C(8), being 116 (1) and 115 (1)°, which are different from the idealized value of 109.48° for tetrahedral geometry.

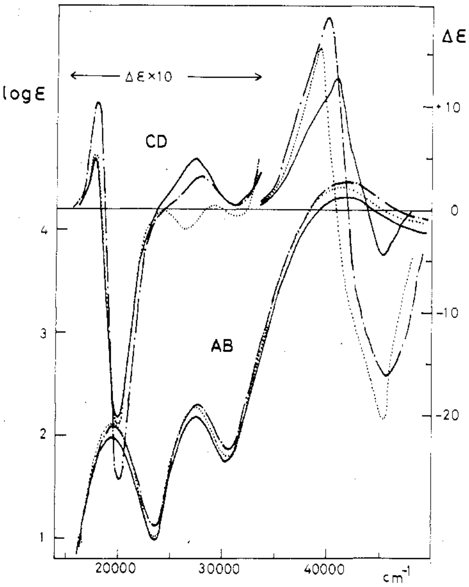

Figure 6. CD spectra of (—) $(-)_{546}$-β-[Co(ox)(*R*,*R*,*R*,*R*-3″,2,3″-tet)]$ClO_4\cdot 3H_2O$, (···) $(-)_{546}$-β-[Co(ox)(*R*,*S*,*R*,*S*-3″,2,3″-tet)]$Cl\cdot 8H_2O$, and (-·-) $(-)_{546}$-β-[Co(ox)(*R*,*S*,*S*,*R*-3″,2,3″-tet)]$Cl\cdot 2H_2O$ in water.

Description of the Unit Cell. The unit cell, Figure 5, consists of two discrete complex cations, the bromide counterions, and the six waters of crystallization. There are N–H···Br hydrogen bonds in the crystal.

Table VI lists some of the important distances outside the complex ion. Hydrogen bonds of the type N–H···Br probably exist between N(2)···Br and N(3)···Br, the N–H···Br angles being 152.5 and 161.7°, respectively. The O(3) atom of the oxalato group is linked to N(1) and N(4) by N–H···O hydrogen bonds at distances of 3.06 and 3.16 Å. The water O(5) atom is associated with the other two water molecules at distances of 2.82 and 2.55 Å. The water O(6) atom is also associated with another water molecule at a length of 2.44 Å. The short approach occurs between oxygen atoms of the oxalato and the water molecules. The positions of the H atoms of the $-NH_2$ and $-NH$ groups are calculated on the assumption that the N–H distance is 1.03 Å.

Though two conformations are possible for the 2,4-pentanediamine parts of this tetraamine, both six-membered chelate rings adopt the chair conformation. Consequently, the six-membered chelate 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 is well-known that the CD sign of the $^1A_1 \rightarrow {}^1A_2$ (E_a) transition (the dominant bond) correlates closely to absolute configurations for *cis*-$[CoO_2N_4]^+$ such as (oxalato)tetraaminecobalt(III) complex ions. This correlation should be confirmed on the basis of X-ray structure analysis. The CD spectra of $(-)_{546}$-β-[Co(ox)(*R*,*R*,*R*,*R*-3″,2,3″-tet)]$^+$,[20] where its enantiomer $(+)_{546}$-β-[Co(ox)(*S*,*S*,*S*,*S*-3″,2,3″-tet)]$^+$ is determined to have the Λ-β configuration in the present X-ray structure analysis, $(-)_{546}$-β-[Co(ox)(*R*,*S*,*S*,*R*-3″,2,3″-tet)]$^+$,[20] and $(-)_{546}$-β-[Co(ox)(*S*,*R*,*R*,*S*-3″,2,3″-tet)]$^+$[20] in an aqueous solution are shown in Figure 6, and they are summarized in Table VII. The CD curves are very similar to one another. These results lead to the conclusion that when the (oxalato)cobalt(III) complexes of 4,7-diazadecane-1,10-diamine (3,2,3-tet) and its C-methylated derivatives give two circular dichroism bands with opposed signs in the first absorption region, an enantiomer which has a lower energy small positive Cotton effect and a higher energy large negative one should be assigned the Δ configuration. This conclusion agrees with the assignment made by analysis of the circular dichroism.[7]

Table VII. Electronic Absorption (AB) and Circular Dichroism (CD) Data: $\tilde{\nu}$ in 10^3 cm^{-1}

complex	AB $\tilde{\nu}$ (log ε)	CD $\tilde{\nu}$ ($\epsilon_l - \epsilon_r$)
$(-)_{546}$-β-[Co(ox)(*R*,*R*,*R*,*R*-3″,2,3″-tet)]$ClO_4\cdot 3H_2O$	19.42 (1.97)	17.70 (+0.50)
		19.92 (−2.02)
	27.40 (2.17)	27.40 (+0.50)
	41.49 (4.30)	40.98 (+13.05)
		45.45 (−4.35)
$(-)_{546}$-β-[Co(ox)(*R*,*S*,*S*,*R*-3″,2,3″-tet)]$Cl\cdot 8H_2O$	19.47 (1.97)	17.73 (+0.53)
		19.92 (−2.09)
	27.40 (2.26)	26.67 (−0.20)
		28.99 (+0.04)
		31.75 (−0.07)
	41.32 (4.40)	39.37 (+15.93)
		45.02 (−20.48)
$(-)_{546}$-β-[Co(ox)(*R*,*S*,*R*,*S*-3″,2,3″-tet)]$Cl\cdot 2H_2O$	19.53 (2.08)	17.94 (+1.05)
		20.08 (−2.64)
	27.47 (2.29)	27.79 (+0.33)
	41.49 (4.45)	40.00 (+18.71)
		45.45 (−16.33)

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Registry No. $(+)_{546}$-β-[Co(ox)(*S*,*S*,*S*,S-3″,2,3″-tet)]$Br\cdot 3H_2O$, 70681-24-2; *trans*-[$CoCl_2$(*S*,*S*,*S*,*S*-3″,2,3″-tet)]ClO_4, 53860-81-4.

Supplementary Material Available: A listing of structure factor amplitudes (7 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) S. Yano, A. Fujioka, M. Yamaguchi, and S. Yoshikawa, *Inorg. Chem.*, **17**, 14 (1978).
(3) A. Kobayashi, F. Marumo, and Y. Saito, *Inorg. Nucl. Chem. Lett.*, **7**, 777 (1971); A. Kobayashi, F. Marumo, and Y. Saito, *Acta Crystallogr., Sect. B*, **28**, 3591 (1972); **29**, 2443 (1973).
(4) Y. Nakayama, S. Ooi, and H. Kuroya, paper presented at the 36th National Meeting of Chemical Society of Japan, spring 1977, Osaka, Japan.
(5) The sign refers to the rotation at 546 nm of [Co(ox)(*R*,*R*,*R*,*R*-3″,2,3″-tet)]$^+$ of our previous letter in *Inorg. Nucl. Chem. Lett.*, **12**, 831 (1976), which was mistaken. $(-)_{546}$-[Co(ox)(*R*,*R*,*R*,*R*-3″,2,3″-tet)]$Br\cdot 3H_2O$ is correct notation.
(6) F. Mizukami, *Bull. Chem. Soc. Jpn.*, **48**, 1205 (1975).
(7) B. Bosnich and J. M. Harrowfield, *Inorg. Chem.*, **14**, 861 (1975).
(8) J. M. Bijvoet, A. F. Peerdeman, and A. J. van Bommel, *Nature (London)*, **168**, 271 (1951).
(9) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, **17**, 781 (1964).
(10) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
(11) "International Tables for X-ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962, pp 270, 276.
(12) Supplementary material.
(13) Computer illustrations were generated by means of ORTEP-II (C. K. Johnson, "ORTEP: A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations", USAEC Report ORNL-3794, revised, 1965; overlap correction, 1971).
(14) R. S. Cohen, C. K. Ingold, and V. Prelog, *Experientia*, **12**, 81 (1956).
(15) *Inorg. Chem.*, **9**, 1 (1970).
(16) N. C. Payne, *Inorg. Chem.*, **11**, 1376 (1972).
(17) P. W. R. Corfield, J. C. Dabrowiak, and E. S. Gore, *Inorg. Chem.*, **12**, 1734 (1973).
(18) K. Matsumoto, S. Ooi, and H. Kuroya, *Bull. Chem. Soc. Jpn.*, **43**, 1903 (1970).
(19) T. Nomura, F. Marumo, and Y. Saito, *Bull. Chem. Soc. Jpn.*, **42**, 1016 (1969).
(20) F. Mizukami, Ph.D. Thesis, The Tohoku University, 1973.