The Crystal Structure of *cis*-β-Λ-Carbonato(*S*,*S*-triethylenetetramine)cobalt(III) Perchlorate: Spontaneous Resolution and Determination of Absolute Configuration

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(Received June 3, 1994)

The single crystal of *cis*-β-Λ-*S*,*S*-[Co(CO_3)(trien)](ClO_4)·H_2O (trien=triethylenetetramine) has spontaneously resolved from the aqueous solution of *cis*-α-[CoCl(NH_3)(trien)](ClO_4)$_2$ containing hydrogencarbonate anion, whose crystal structure has been determined by X-ray diffraction method. The complex crystallizes in the monoclinic space group $P2_1$ with $a=7.410(1)$, $b=12.354(3)$, $c=8.676(1)$ Å, $\beta=108.88(1)°$, and $Z=2$. The final R and R_w values for the 3056 observed reflections with $I_o>3\sigma(I_o)$ are 0.045 and 0.055, respectively. The tetradentate ligand, trien, is linked to the cobalt atom in *cis*-β-configuration, and the carbonato anion is coordinated to the metal atom as a didentate ligand. The Co–N bond lengths are 1.904(6), 1.928(4), 1.941(4), and 1.955(5) Å, and the two Co–O bond lengths are both 1.909(4). The absolute configuration of the complex cation can be designated as Λ(λλδ) and those about two secondary nitrogen atoms are both *S*.

The complex [CoCl(NH_3)(trien)]$^{2+}$ (trien=triethylenetetramine) with *cis*-α-configuration is specifically synthesized in the usual way,[1] which is obtained as a mixture of two isomers due to the arrangement of two terminal chelate rings into optical enantiomerism, Δ and Λ.[2] We have recently carried out the kinetic study of the substitution reaction of this complex to [Co(CO_3)(NH_3)(trien)]$^+$, in which the carbonato ion was demonstrated to coordinate to metal ion as a monodentate ligand.[3] After the standing of an aqueous solution containing this complex for several weeks, only one kind of single crystal was isolated. Interestingly enough, the X-ray crystal structure analysis of the product complex revealed this crystallization to proceed with a spontaneous resolution characteristic. This paper will be concerned with a detailed investigation on the structure of this optically active complex.

Experimental

Orange-red crystals of the title compound suitable for the X-ray structure analysis were obtained from the reaction mixture of *cis*-α-[CoCl(NH_3)(trien)](ClO_4)$_2$ with hydrogencarbonate ion in an aqueous solution at pH 8.2—9.0. Crystal data and experimental details are summarized in Table 1. Diffraction data were obtained with an Enraf–Nonius CAD4-EXPRESS four-circle automated diffractometer. The crystal was mounted on the glass capillary. The reflection intensities were monitored by three standard reflections at every 2 h, and the decay of intensities were within 2%. Reflection data were corrected for Lorentz and polarization effects. An empirical absorption correction, based on ψ scans, was applied.

The structure was solved by the heavy-atom method and refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculations. Refinement was continued until all shifts were smaller than one-third of the parameters involved. Atomic scattering factors and anomalous dispersion terms were taken from the International Tables for X-Ray Crystallography.[4] All hydrogen atoms were located from difference Fourier maps, and their parameters were isotropically refined. The absolute configuration of the complex ion was determined by the anomalous dispersion method. The final R and R_w values were 0.045 and 0.055 for the Λ form and 0.059 and 0.065 for the Δ form, respectively, which indicated that the complex ion *cis*-β-[Co(CO_3)(trien)]$^+$ has the absolute configuration Λ as illustrated in Fig. 1. The weighting scheme $w^{-1}=(\sigma^2(F_o)+(0.015F_o)^2)$ was employed for the crystal. The final difference Fourier map did not show any significant features. The calculations were performed on a Micro VAX-3100 computer by using the program system SDP-MolEN.[5]

The final atomic parameters for non-hydrogen atoms are given in Table 2. Tables of the anisotropic thermal parameters, coordinates of the hydrogen atoms, and the observed and calculated structure factors have been deposited as Doc-

Table 1. Crystallographic Data and Experimental Details for [Co(CO_3)(trien)]ClO_4·H_2O

Formula	$CoClO_7N_4C_7H_{18}$·H_2O
FW	362.48
Color	Orange red
Crystal size/mm^3	0.20×0.20×0.15
Crystal system	Monoclinic
Space group	$P2_1$
a/Å	7.410(1)
b/Å	12.354(3)
c/Å	8.676(1)
β/deg	108.88(1)
V/Å^3	751.5(2)
Z	2
Collecn range	$0\leq h\leq 9$, $-15\leq k\leq 15$, $-10\leq l\leq 10$
Scan mode	ω–2θ
2θ range/deg	2—55
D_X(Mg m^{-3})	1.602
Abs. coeff. μ/mm^{-1}	13.58 (Mo $K\alpha$)
λ/Å	0.71073
Transm factors	0.712—0.994
T/K	293
Refls. obsd	5682
Refls. used($I_o>3\sigma(I_o)$)	3056
R/%	0.045
R_w/%	0.055

Table 2. Final Positional Parameters (×10^4) and B_{eq} Values (Å) for the Non-hydrogen Atoms of [Co(CO$_3$)(trien)]ClO$_4$·H$_2$O

Atom	x	y	z	B_{eq}[a)]
Co[b)]	0.96538(9)	0	0.04852(7)	1.64(1)
Cl	0.6392(2)	−0.2913(1)	0.3988(2)	2.84(3)
O(1)	0.8260(8)	−0.3116(6)	0.5060(8)	5.8(2)
O(2)[c)]	0.524(3)	−0.279(2)	0.473(2)	10.9(7)
O(3)[c)]	0.636(2)	−0.258(1)	0.258(1)	6.2(3)
O(4)[c)]	0.556(2)	−0.394(1)	0.378(2)	7.3(4)
O(5)[c)]	0.657(2)	−0.197(1)	0.304(2)	8.5(3)
O(6)[c)]	0.564(3)	−0.368(2)	0.274(2)	13.0(5)
O(7)[c)]	0.526(2)	−0.229(1)	0.484(1)	7.2(3)
O(1W)	0.4464(7)	0.2910(5)	0.1899(7)	4.8(1)
C(1c)	0.8331(9)	0.1634(4)	0.0918(8)	2.4(1)
O(1c)	0.7903(5)	0.0679(3)	0.1382(5)	2.49(8)
O(2c)	0.9629(5)	0.1532(3)	0.0203(5)	2.32(8)
O(3c)	0.7627(7)	0.2508(3)	0.1092(6)	3.7(1)
N(1)	0.7787(7)	−0.0181(4)	−0.1663(6)	2.6(1)
C(2)	0.873(1)	−0.0460(7)	−0.2834(8)	4.0(2)
C(3)	1.0743(9)	−0.0028(8)	−0.2247(6)	3.7(1)
N(4)	1.1533(7)	−0.0315(4)	−0.0515(6)	2.4(1)
C(5)	1.3306(9)	0.0252(5)	0.0417(9)	3.3(1)
C(6)	1.3606(8)	0.0014(7)	0.2171(8)	3.4(1)
N(7)	1.1750(7)	0.0118(4)	0.2493(5)	2.46(9)
C(8)	1.146(1)	−0.0698(6)	0.3634(8)	3.4(2)
C(9)	1.086(1)	−0.1746(5)	0.2691(8)	3.0(1)
N(10)	0.9326(7)	−0.1474(4)	0.1169(6)	2.4(1)

a) Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq} = (4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$. b) The y coordinate of Co is fixed. c) The O atoms of perchlorate anion were refined with 0.5 occupancy.

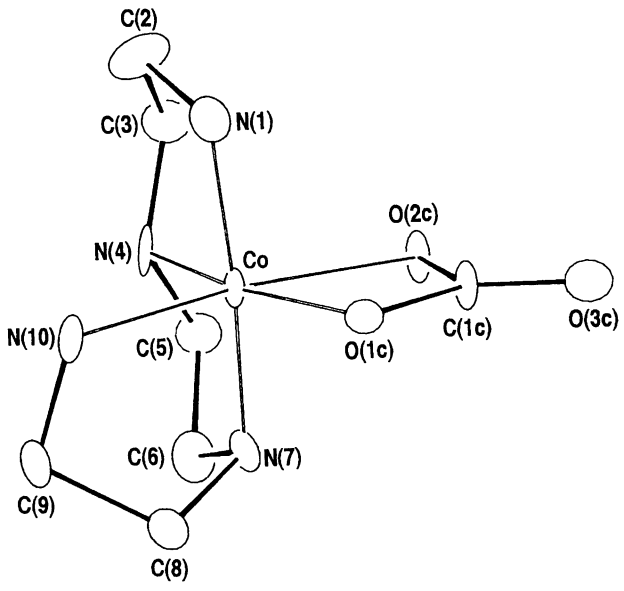

Fig. 1. A perspective drawing of [Co(CO$_3$)(trien)]$^+$ cation.

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Results and Discussion

A perspective drawing of the complex ion *cis*-β-[Co(CO$_3$)(trien)]$^+$, also showing the atomic numbering scheme, is presented in Fig. 1. It correctly represents the absolute configuration. The bond lengths and angles are given in Table 3. A molecule of trien is linked to the central cobalt atom in *cis*-β-coordination. The cobalt atom is surrounded by four nitrogen atoms of trien and two oxygen atoms of carbonato ion at the apices of a slightly distorted octahedron.

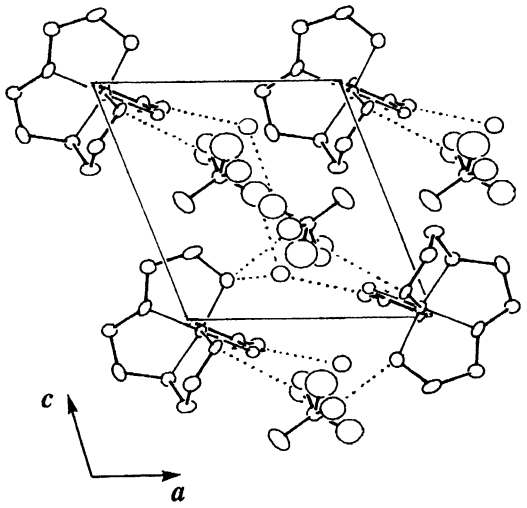

Fig. 2. A projection of the crystal structure along the *b*-axis. Broken lines indicate hydrogen bondings.

Table 3. Selected Bond Lengths (Å) and Valence Angles (deg) in $[Co(CO_3)(trien)]ClO_4 \cdot H_2O$

Co–O(1c)	1.909(4)	Co–O(2c)	1.909(4)
Co–N(1)	1.941(4)	Co–N(4)	1.904(6)
Co–N(7)	1.928(4)	Co–N(10)	1.955(5)
O(1c)–C(1c)	1.318(7)	O(2c)–C(1c)	1.309(9)
O(3c)–C(1c)	1.229(7)	N(1)–C(2)	1.45(1)
N(4)–C(3)	1.468(7)	N(4)–C(5)	1.477(7)
N(7)–C(6)	1.495(9)	N(7)–C(8)	1.476(9)
N(10)–C(9)	1.476(7)	C(2)–C(3)	1.51(1)
C(5)–C(6)	1.49(1)	C(8)–C(9)	1.518(9)
O(1c)–Co–O(2c)	68.7(2)	O(1c)–Co–N(1)	94.3(2)
O(1c)–Co–N(4)	165.7(2)	O(1c)–Co–N(7)	93.1(2)
O(1c)–Co–N(10)	96.8(2)	O(2c)–Co–N(1)	90.9(2)
O(2c)–Co–N(4)	97.0(2)	O(2c)–Co–N(7)	90.7(2)
O(2c)–Co–N(10)	165.1(2)	N(1)–Co–N(4)	86.4(2)
N(1)–Co–N(7)	172.6(2)	N(1)–Co–N(10)	93.7(2)
N(4)–Co–N(7)	86.2(2)	N(4)–Co–N(10)	97.4(2)
N(7)–Co–N(10)	86.5(2)	Co–O(1c)–C(1c)	90.4(4)
Co–O(2c)–C(1c)	90.7(3)	O(1c)–C(1c)–O(2c)	110.2(5)
O(1c)–C(1c)–O(3c)	126.5(7)	O(2c)–C(1c)–O(3c)	123.3(6)
Co–N(1)–C(2)	110.1(4)	Co–N(4)–C(3)	108.0(4)
Co–N(4)–C(5)	107.8(4)	Co–N(7)–C(6)	110.2(4)
Co–N(7)–C(8)	107.8(4)	Co–N(10)–C(9)	110.3(4)
C(3)–N(4)–C(5)	115.8(5)	C(6)–N(7)–C(8)	114.1(5)

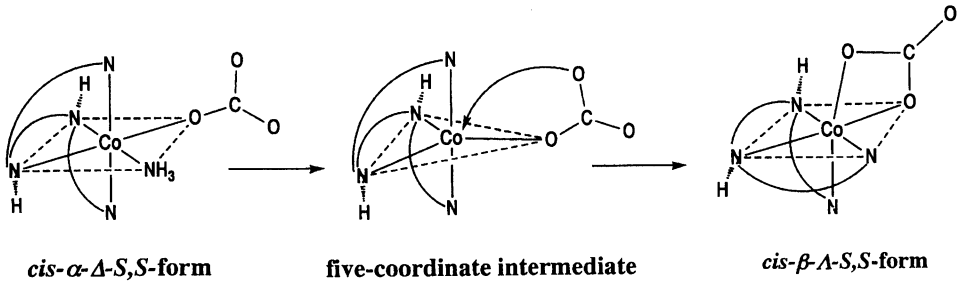

Fig. 3. Possible mechanism of the removal of NH_3 and isomerization of the *cis*-α- to the *cis*-β-form involving a five coordinate intermediate.

As discerned from Table 3, the two secondary nitrogen atoms, N(4) and N(7), (1.904(6) and 1.928(4) Å, respectively), are coordinated to the cobalt atom with significantly shorter lengths than the other two terminal nitrogen atoms, N(1) and N(10), (1.941(4) and 1.955(5) Å, respectively), although generally the primary amine (1.952—1.976 Å)[6] and the secondary amine (1.947—1.986 Å)[6] coordinate comparably to cobalt(III) atom. Especially, one of the two secondary nitrogen atoms, N(4), is strongly bonded to the cobalt atom. Such a shortening is also observed for the secondary nitrogen atoms in *cis*-β-$[Co(CO_3)(3S,8S\text{-}Me_2\text{-}trien)]ClO_4$ (Me_2-trien=dimethyltriethylenetetramine)[7] and *trans*-$[Co(NO_2)_2(3,8\text{-}Me_2\text{-}trien)]^+$.[8] The average angle subtended at the cobalt atom by the chelate rings is compressed to 86.4°, which is comparable with those observed in other trien structures.[9] The three five-membered chelate rings adopt the gauche conformation, and have absolute configurations λ, λ, and δ, respectively. The carbonato group bonds to the metal atom in a didentate coordination, and the two Co–O bonds exhibit almostly same lengths (1.909(4) and 1.909(4) Å), which are in the range reported hitherto (1.893—1.916 Å).[6] The carbonato group is almost planar, and the dihedral angle between the planes by Co, N(4) and N(10) and Co, O(1c) and O(2c) is 3.8°.

The unit cell of crystal contains two discrete complex cations, two perchlorate anions and two water molecules, which are linked by three-dimensional hydrogen bond networks each other. Projection of the crystal structure along the *b*-axis is shown in Fig. 2. Selected hydrogen bond distances are listed in Table 4. The complex cations, which are related by the two-fold screw translation along the *b* axis each other, are linked to the adjacent water molecule through hydrogen bonds between the oxygen atom O(3c) of a carbonato group and water molecule O(1w), 2.858(8) Å, and between the amino nitrogen atom N(1) and O(1w), 2.700(8) Å. The complex cations form an infinite chain along the *b* axis. The perchlorate anion is disordered around Cl–

Table 4. Interatomic Distances (Å) Less than 3.0 Å

O(1w)···O(2)	2.99
O(1w)···O(3c)	2.70
O(1w)···O(7)	2.78
O(1w)···N(1)	2.86
O(4)···N(1)	2.99

O(1) axis.

Interestingly, this crystal spontaneously resolved, whose absolute configuration can be designated as $\Lambda(\lambda\lambda\delta)$ and those about the two secondary nitrogen atoms are both *S*. The absolute structure of this complex is much the same as that in *cis*-β-$[Co(CO_3)(3S,8S\text{-}Me_2\text{-trien})]ClO_4$.[7] The CD spectrum of the complex solution was inactive, which indicates that the complex solution was a mixture of several geometrical or mirror-image isomers and that the other complexes with different configuration or conformation were not isolated as a single crystal.

As described above, the complex structure is *cis*-β-*S*,*S*-form with Λ configuration, although the starting complex *cis*-α-$[CoCl(NH_3)(trien)]^{2+}$ is a mixture of two kinds of optical isomers, *cis*-α-*R*,*R*-, *cis*-α-*S*,*S*-. Consequently, the crystal isolated here means that the starting compound is *cis*-α-Δ-*S*,*S*-form. Because the *cis*-β-Λ-*S*,*S*-form is not formed except from the *cis*-α-Δ-*S*,*S*-form, unless drastic configurational rearrangement of trien has occurred about metal atom in the solution. On the basis of the above facts, the removal of an ammine molecule and the configurational rearrangement of trien may be explained as follows.

Generally, in an aqueous solution containing HCO_3^-, the complex $[CoCl(NH_3)(trien)]^{2+}$ is hydrolyzed to $[Co(OH)(NH_3)(trien)]^{2+}$ or $[Co(H_2O)(NH_3)(trien)]^{3+}$, in which the latter is immediately changed to the former by proton abstraction.[9] Next, the complex $[Co(OH)(NH_3)(trien)]^{2+}$ is substituted by HCO_3^- to give $[Co(CO_3)(NH_3)(trien)]^+$ having the carbonato anion as a monodentate ligand.[3] The standing of the complex solution for several weeks resulted in the removal of NH_3 and the rearrangement of trien about the metal atom from *cis*-α- to *cis*-β-form. This rearrangement of trien is considered to be carried out via the five-coordinate trigonal bipyramidal intermediate followed by the removal of NH_3, as shown in Fig. 3, and then one of the two non-coordinating carbonato oxygen atoms attacks the cobalt atom to give the *cis*-β-$[Co(CO_3)(trien)]^+$. The significantly shorter Co–N(4) bond mentioned above may indicate the higher stability of the *cis*-β-form in this complex in comparison with the *cis*-α-form.

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