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Cobalt(III) Complexes with $[N_{6-n}X_n]$-Type Ligands. VIII.[1] Preparation and Properties of Isomers of the (Salicylaldoximato)(triethylenetetramine)cobalt(III) Complexes and Crystal Structure of *cis*-β_1-(*RS*, *SR*)-[Co(salal)(trien)]Cl·(CH_3COCH_3)·$2H_2O$

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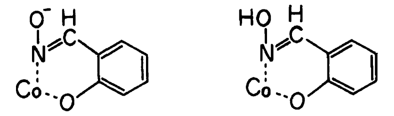
The title complexes of *cis*-β_1-(*RR*,*SS*)-, *cis*-β_1-(*RS*,*SR*)-, *cis*-β_2-(*RR*,*SS*)-, and *cis*-β_2-(*RS*,*SR*)-[Co(**A**)(trien)]Cl·nH_2O and *cis*-β_1-(*RR*,*SS*)-, *cis*-β_1-(*RS*,*SR*)-, and *cis*-β_2-(*RR*,*SS*)-[Co(**B**)(trien)]Cl_2 have been obtained from a reaction mixture of *cis*-α-[$CoCl_2$(trien)]Cl, Ag_2O, and salicylaldoxime (Chart 1).



(A) (B)

Chart 1.

Separations of the **A**- and **B**-type complexes, and of the geometrical isomers of *cis*-β_1 and β_2, as well as those of the diastereoisomers of (*RR*,*SS*) and (*RS*,*SR*) were attempted by using Dowex 50W-X2 column chromatography. The **B**-type complexes were obtaind from the reaction mixture of the corresponding **A**-type complexes and hydrochloric acid. The structure of *cis*-β_1-(*RS*,*SR*)-[Co(**A**)(trien)]Cl·(CH_3COCH_3)·$2H_2O$ has been confirmed by an X-ray analysis. Crystal data: $CoC_{16}H_{33}N_5O_5Cl$, orthorhombic, $Pb2_1a$, $a=14.091(2)$, $b=22.385(3)$, $c=7.011(2)$ Å, $V=2211.5(6)$ Å^3, $Z=4$, and $R=0.076$. A property between **A**- and **B**-type complexes has been compared in the IR, NMR spectra, and electric conductivity in aqueous solution; i.e., the CH=N streching vibrations (ca. 1590 cm^{-1}) of **A**-type complexes have a lower wavenumber than those (ca. 1600 cm^{-1}) of **B**-type complexes. The chemical shifts ($\delta=148$—150) of the CH=N carbon signal of **A**-type complexes are at a higher field than those ($\delta=160$—162) of **B**-type complexes in D_2O. The chemical shifts ($\delta=7.9$—8.0) of the CH=N proton signal of **A**-type complexes are at a higher field than those ($\delta=8.2$—8.4) of **B**-type complexes in D_2O. The electric conductivities in aqueous solutions of **A**- and **B**-type complexes were ca. 120 and ca. 220 S cm^2 mol^{-1}, respectively. The absorption spectra of *cis*-β-(*RS*,*SR*)-isomers and the corresponding (*RR*,*SS*)-isomers showed two peaks at around 350 and 540 nm and three peaks at around 350, 470, and 540 nm, respectively.

Previously, we have described the preparation, properties, and geometrical isomers of mixed-ligand (trien)cobalt(III) complexes with salicylato,[2,3] thiosalicylato,[4] salicylaldehydato,[5,6] and salicylamidato[1] ligands. However, the preparation and properties of mixed-ligand (amine)(salicylaldoximato)cobalt(III) complexes have not been of concern. In the case of metal complexes with the salicylaldoxime (2-hydroxybenzaldehyde oxime) ligand, **A**-, **B**-, and **C**-types can be formed for the chelated ligand in complexes, because the oxime group (–CH=N–OH) of the salicylaldoxime ligand can coordinate to a metal atom through a nitrogen (**A**- and **B**-types) or an oxygen atom (**C**-type), as shown in Fig. 1.

Although many bis(salicylaldoximato)metal complexes having the **B**-type structure have been reported concerning their preparation,[7—10] properties,[11—13] and X-ray diffraction,[14—16] the corresponding **A**- and **C**-type structures have not been reported. Thus, the

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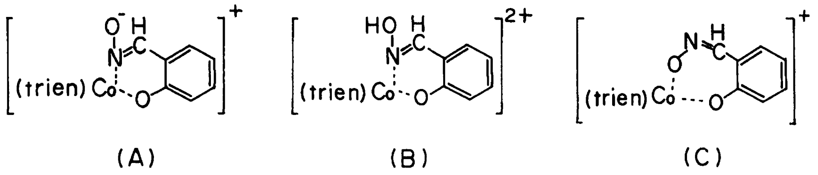

Fig. 1. Configurations of the **A**-, **B**-, and **C**-type complexes of (salicylaldoximato)(triethylenetetramine)cobalt(III) complex.

present paper deals with the preparation and properties of **A**- and **B**-type complexes of the mixed-ligand (salicylaldoximato)(triethylenetetramine)cobalt(III), and with an X-ray crystallographic analysis of the **A**-type complex.

Experimental

Measurements. Electric conductivities were determined using a CM-40S conductivity meter (TOA) in an aqueous solutions at room temperature. IR spectra were recorded in KBr disks on a Hitachi 270-30 spectrophotometer. Visible absorption spectra were recorded in water on a Shimadzu UV-210 recording spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a JNM-FX400 FT NMR spectrometer (JEOL). Melting points were measured with an MP-500D apparatus (Yanako).

Preparation of Complexes. ***cis*-β_2-(*RS*,*SR*)-(Salicylaldoximato)(triethylenetetramine)cobalt(III) Chloride Dihydrate (1), *cis*-β_1-(*RS*,*SR*)-(Salicylaldoximato)(triethylenetetramine)cobalt(III) Chloride (2), *cis*-β_1-(*RR*,*SS*)-(Salicylaldoximato)(triethylenetetramine)cobalt(III) Chloride Hydrate (3), *cis*-β_2-(*RR*,*SS*)-(Salicylaldoximato)(triethylenetetramine)cobalt(III) Chloride (4), *cis*-β_1-(*RS*,*SR*)-(Salicylaldoximato)(triethylenetetramine)cobalt(III) Dichloride (5), and *cis*-β_1-(*RR*,*SS*)-(Salicylaldoximato)(triethylenetetramine)cobalt(III) Dichloride (6):** *cis*-α-[CoCl$_2$(trien)]Cl (10.0 g, 32.1 mmol) was added to moistend fresh Ag_2O, which was made from silver nitrate (10.9 g, 64.2 mmol) and potassium hydroxide (3.6 g, 64.2 mmol). The mixture was stirred for several minutes at room temperature; then, 10 cm^3 of water was added to the mixture. After the mixture had been stirred for about 30 min at 60 °C, the precipitated silver chloride was filtered off and washed with a small amount of water. A methanol solution (40 cm^3) of salicylaldoxime (4.4 g, 32.1 mmol) was added, drop by drop, to a reddish-violet solution (pH=8.6) at 50 °C. After the solution had been stirred for 6 h at 50 °C it was concentrated on a rotary evaporator. The separation of complexes **1**—**6** was achieved by using a column (ϕ 3.0 cm ×40 cm) of ion-exchange resin (Dowex 50W-X2, Na$^+$ form, 100—200 mesh). Upon elution with 0.1 mol dm^{-3} NaCl, the effluents of the first russet band (complex **1**), second russet band (complex **2**), third reddish-brown band (complex **3**), and fourth reddish-brown band (complex **4**) were collected and concentrated, respectively. Then, the fifth russet band (complex **5**) and sixth reddish-brown band (complex **6**) were eluted with 0.5 mol dm^{-3} NaCl and concentrated, respectively. Complexes **1**—**6** were recrystallized from methanol–ether or ethanol–acetone. Yields: 0.58 g (4.4%) for **1**, 2.16 g (18.0%) for **2**, 0.54 g (4.3%) for **3**, 1.02 g (8.4%) for **4**, 0.21 g (1.6%) for **5**, and 0.45 g (3.5%) for **6**. Found **1**: C, 38.20; H, 6.46; N, 16.91; Cl, 8.77%. Calcd for $C_{13}H_{23}N_5O_2ClCo\cdot 2H_2O$ (MW 411.78): C, 37.91; H, 6.61; N, 17.01; Cl, 8.61%. Found **2**: C, 41.82; H, 6.42; N, 18.72; Cl, 9.18%. Calcd for $C_{13}H_{23}N_5O_2ClCo$ (MW 375.74): C, 41.55; H, 6.17; N, 18.64; Cl, 9.43%. Found **3**: C, 39.58; H, 6.78; N, 18.02; Cl, 9.25%. Calcd for $C_{13}H_{23}N_5O_2ClCo\cdot H_2O$ (MW 393.76): C, 39.65; H, 6.41; N, 17.79; Cl, 9.00%. Found **4**: C, 41.76; H, 6.37; N, 18.37; Cl, 9.17%. Calcd for $C_{13}H_{23}N_5O_2ClCo$ (MW 375.74): C, 41.55; H, 6.17; N, 18.64; Cl, 9.43%. Found **5**: C, 37.50; H, 5.76; N, 17.31; Cl, 17.00%. **6**: C, 37.61; H, 6.09; N, 16.71; Cl, 16.96%. Calcd for $C_{13}H_{24}N_5O_2Cl_2Co$ (MW 412.20): C, 37.88; H, 5.87; N, 16.99; Cl, 17.20%. IR (NH_2 twist.): **1**: 1005, 1030, 1060, 1070 cm^{-1}. **2**: 1005, 1030, 1062, 1086 cm^{-1}. **3**: 1004, 1035, 1060, 1085 cm^{-1}. **4**: 999, 1031, 1050, 1075 cm^{-1}. **5**: 1000, 1040, 1068, 1080 cm^{-1}. **6**: 1000, 1010, 1038, 1060 cm^{-1}. Dp: 212—214 for **1**, 219—220 for **2**, 217—218 for **3**, 217—218 for **4**, 199—201 for **5**, and 203—204 °C for **6**.

Preparation of *cis*-β_2-(*RR*,*SS*)-(Salicylaldoximato)(triethylenetetramine)cobalt(III) Dichloride (7): Complex **4** (1.0 g, 2.66 mmol) was dissolved in 3 cm^3 of 2 mol dm^{-3} HCl; the solution was then stirred for 10 min at room temperature. The solution was poured onto a column of ion-exchange resin (Dowex 50W-X2). Elution with 0.3 mol dm^{-3} NaCl produced one band. Complex **7** was eluted with 0.5 mol dm^{-3} NaCl and concentrated. Yield: 0.81 g (74.1%). Found: C, 38.02; H, 6.12; N, 16.74; Cl, 17.49%. Calcd for $C_{13}H_{24}N_5O_2Cl_2Co$ (MW 412.20): C, 37.88; H, 5.87; N, 16.99; Cl, 17.20%. IR (NH_2 twist.): 995, 1026, 1038, 1060, 1081 cm^{-1}. Dp: 217—218 °C.

Preparation of Complex 5 from 2 and Complex 6 from 3: Complex **5** was prepared from **2** (0.5 g, 1.33 mmol) and 2 mol dm^{-3} HCl (2 cm^3) in the same manner as in the preparation of **7**. Complex **6** was also obtained from a mixture of **3** (0.5 g, 1.27 mmol) and 2 mol dm^{-3} HCl (2 cm^3). Yields: 0.41 g (74.8%) for **5**, 0.38 g (72.6%) for **6**.

X-Ray Crystallography. Complex **2** was recrystallized from aqueous acetone. A deep-red plate having approximate dimensions of 0.50×0.08×0.20 mm was sealed in a thin-walled glass capillary since the single crystal of **2** is unstable in air. X-Ray data of **2** was collected with graphite-monochromated Mo $K\alpha$ radiation (λ=0.71069 Å) on a Rigaku AFC-5R diffractometer at 20 °C. The unit cell parameters were obtained by a least-squares refinement of 25 reflections ($25 \leq 2\theta \leq 30°$). The intensities of three standard reflections monitored every 150 reflections showed no appreciable decay during the data collection. No absorption correction was made.

The crystal structure was solved by standard heavy-atom procedures. The positional and thermal parameters were refined by a block-diagonal-matrix least-squares method.

The minimized function was $\sum w(|F_o|-|F_c|)^2$, where $w^{-1}=\sigma^2(|F_o|)+(0.015|F_o|)^2$. All hydrogen atoms, except for the solvent molecules, were located in the calculated positions (C–H, N–H=1.09 Å for trien, C–H=1.08 Å for salicylaldoximato anion). Although these H atoms were included in the least-squares calculation, their parameters were not refined. Each H atom was assigned an isotropic temperature factor equal to that of the atom to which it is bonded. No correction was made for secondary extinction. The atomic scattering factors for neutral atoms, with a correction for the anomalous dispersion of Co^0 and Cl^0, were used throughout the analysis.[17)] Computational work was carried out by using standard programs in UNICS III[18)] and ORTEP.[19)] Further crystallographic data are given in Table 1. Listings of the non-hydrogen atom coordinates are given in Table 2, and selected bond distances and angles are summarized in Table 6. Anisotropic thermal parameters (Table S1), derived hydrogen positions (Table S2), and full listings of bond distances and angles (Table S3) are deposited as Document No. 68009 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

The abbreviations of the octahedral (salicylaldoximato)(triethylenetetramine)cobalt(III) complexes in this research are listed in Table 3.

Preparation and Properties of Complexes. Complexes **1**—**6** were obtained from a reaction mixture of *cis*-*α*-[$CoCl_2$(trien)]Cl, Ag_2O, and salicylaldoxime. Complexes **1**—**6** were separated by Dowex 50W-X2 column chromatography. The formation ratios of **1**, **2**, **3**, **4**, **5**, and **6** are ca. 3 : 11 : 3 : 5 : 1 : 2, respectively. Complexes **1** and **3** isomerize to **4** and **2**, respectively, in aqueous solution at room temperature. The isomerization of **1** is very fast, though that of **3** is slow. Complexes **5**, **6**, and **7** were obtained from the reaction mixture of complexes **2**, **3**, and **4** and 2 mol dm^{-3} HCl, respectively. The colors of **1**, **2**, and **5** are brownish-violet, and those of **3**, **4**, **6**, and **7** are reddish-brown. Complexes **1**—**7** were soluble in water, alcohols, dimethyl sulfoxide, but were not soluble in common organic solvents, such as acetone and ether.

Table 1. Crystallographic Data for *cis*-β_1-(*RS*,*SR*)-[Co(**A**)(trien)]Cl·(CH_3COCH_3)·$2H_2O$

Formula	$CoC_{16}H_{33}N_5O_5Cl$
Formula weight	469.86
Crystal system	Orthorhombic
Space group	$Pb2_1a$
a/Å	14.091(2)
b/Å	22.385(3)
c/Å	7.011(2)
V/Å^3	2211.5(6)
Z	4
D_{calcd}/g cm^{-3}	1.41
Scan range/°	1.0+0.4 tan θ
Scan mode	ω–2θ
Scan speed/° min^{-1}	6
$2\theta_{max}$/°	60
No. of unique reflcns	3342
No. of obsd reflcns	1978, [$|F_o|>3\sigma(|F_o|)$]
R	0.076
R_w	0.062

Table 2. Fractional Coordinates and Isotropic Thermal Parameters for Non-Hydrogen Atoms of Complex **2**

Atom	x	y	z	B_{eq}/Å^2
Co	0.1623(1)	0.0000(1)	−0.0958(2)	2.04(2)
Cl	−0.0567(2)	−0.0975(2)	0.3375(4)	4.3(1)
N(1)	0.2426(6)	−0.0692(4)	−0.0623(1)	3.0(2)
C(2)	0.1933(8)	−0.1233(4)	−0.1378(1)	3.3(3)
C(3)	0.0902(8)	−0.1138(5)	−0.1320(1)	3.9(3)
N(4)	0.0733(6)	−0.0527(3)	−0.207(1)	2.8(2)
C(5)	−0.0243(7)	−0.0279(5)	−0.183(2)	3.9(3)
C(6)	−0.0191(7)	0.0374(5)	−0.227(1)	3.3(3)
N(7)	0.0680(5)	0.0639(3)	−0.138(1)	2.3(2)
C(8)	0.0480(7)	0.0930(5)	0.053(1)	3.4(3)
C(9)	0.0350(7)	0.0429(4)	0.201(1)	2.9(3)
N(10)	0.1038(4)	−0.0041(5)	0.1637(9)	2.6(2)
O(1)	0.2510(4)	0.0533(3)	0.0263(8)	2.6(2)
O(2)	0.1912(5)	−0.0219(3)	−0.4846(9)	3.0(2)
C(11)	0.2993(7)	0.1081(5)	−0.252(1)	3.1(3)
C(12)	0.2831(6)	0.1033(4)	−0.053(1)	2.9(3)
C(13)	0.3055(7)	0.1516(4)	0.061(2)	3.3(3)
C(14)	0.3434(8)	0.2029(4)	−0.015(2)	4.2(3)
C(15)	0.3630(8)	0.2086(5)	−0.212(2)	4.1(3)
C(16)	0.3399(8)	0.1603(5)	−0.323(2)	3.9(3)
C(17)	0.2709(6)	0.0609(4)	−0.384(1)	2.5(2)
N(18)	0.2170(5)	0.0173(3)	−0.343(1)	2.3(2)
OA(1)	0.0859(8)	0.1529(4)	0.554(1)	6.8(3)
CA(1)	0.098(1)	0.2366(7)	0.759(2)	7.0(5)
CA(2)	0.0998(8)	0.2039(5)	0.564(2)	4.7(4)
CA(3)	0.122(1)	0.2442(8)	0.401(2)	8.1(6)
OW(1)	0.2779(5)	−0.1106(3)	0.3522(9)	3.9(2)
OW(2)	0.1177(7)	−0.1893(5)	−0.621(2)	7.9(4)

The absorption spectra of **1**—**7** were measured in water (Table 3). The absorption bands at ca. 340—360 nm were assigned to the salicylaldoximato ligand, while the bands at ca. 533—545 nm were assigned to the first absorption band.[3)] The IR spectra of **1**—**7** showed C=N stretching vibrations at 1590—1600 cm^{-1} (Table 3). The ^{13}C NMR spectra of complexes **1**—**7** were measured in D_2O and 1.8 mol dm^{-3} D_2SO_4 (Table 4). Seven signals at δ=116—162 were assigned to the carbons of the coordinated salicylaldoximato ligand. The signals at δ=41—58 were assigned to the methylene carbons of the coordinated trien ligand. The ^1H NMR spectra of complexes **1**—**7** were measured in D_2O and 1.8 mol dm^{-3} D_2SO_4; the data are collected in Table 5. The signals at δ=6.7—7.4 (4H) were assigned to the ring protons of the salicylaldoximato ligand. The signals at δ=2.3—3.7 (12H) and 3.5—6.8 (6H) were assigned to the methylene and amine protons of the trien ligand, respectively. The ^1H and ^{13}C NMR spectra of **2**, **3**, and **4** are similar to those of **5**, **6**, and **7**, respectively, in 1.8 mol dm^{-3} D_2SO_4. The assignments of the NH- and NH_2-side methylene protons are based on ^1H–^1H and ^{13}C–^1H COSY measurements.

Table 3. The Abbreviations and Some Physical Properties of Complexes **1**—**7**

Complex no.	Electric conductivity of aqueous solution	IR spectra ν(C=N)	Absorption bands in water λ/nm		
	(S cm^2 mol^{-1})	cm^{-1}	(ε/cm^{-1} mol^{-1} dm^3)		
1 *cis*-β_2-(*RS*,*SR*)-[Co(**A**)trien]Cl·2H$_2$O	110	1594(s)	340(3140)		545(185)
2 *cis*-β_1-(*RS*,*SR*)-[Co(**A**)trien]Cl	116	1592(s)	355(3310)		537(220)
3 *cis*-β_1-(*RR*,*SS*)-[Co(**A**)trien]Cl·H$_2$O	115	1594(s)	350(3500)	470(210)	545(200)
4 *cis*-β_2-(*RR*,*SS*)-[Co(**A**)trien]Cl	124	1592(s)	340(2940)	470(200)	540(180)
5 *cis*-β_1-(*RS*,*SR*)-[Co(**B**)trien]Cl$_2$	225	1603(vs)	355(3150)		533(225)
6 *cis*-β_1-(*RR*,*SS*)-[Co(**B**)trien]Cl$_2$	228	1603(vs)	360(3030)	470(255)	545(205)
7 *cis*-β_2-(*RR*,*SS*)-[Co(**B**)trien]Cl$_2$	220	1601(vs)	360(2670)	470(240)	540(190)

Table 4. ^{13}C NMR Spectra of Complexes **1**—**7**

Complex no.	Trien[a] δ NH$_2$-side methylene carbons		NH-side methylene carbons				Salicylaldoximato[a] δ							Solvent
	[C-2,	C-9]	[C-3,	C-5,	C-6,	C-8]	C-11	C-12	C-13	C-14	C-15	C-16	C-17	
1	43.6	46.3	51.6		55.3	57.2	121.5	160.0	122.1	132.2	118.1	131.2	148.9	1)
2	43.0	45.8	51.5	51.7	54.8	56.6	120.4	160.1	121.7	132.6	117.4	131.6	149.2	1)
	43.7	46.9	52.1	52.3	54.7	57.3	116.8	162.5	122.7	136.1	117.9	134.2	162.2	2)
3	42.9	43.9	53.9		55.5		121.1	160.3	121.8	132.3	117.6	131.4	148.4	1)
	43.6	43.7	54.2	54.6	55.7	56.3	116.3	162.1	122.6	135.8	117.6	134.1	161.3	2)
4	41.8	48.1	48.5	49.1	53.3	53.7	121.6	160.8	122.0	132.7	117.9	131.4	150.0	1)
	41.6	48.1	48.1	49.4	53.2	53.4	116.3	162.3	122.3	135.5	117.2	133.5	161.6	2)
5	43.6	46.7	51.9	52.0	54.6	57.1	116.9	162.5	122.6	136.0	117.8	134.0	161.3	1)
	43.7	46.2	51.5	51.7	54.1	56.6	116.2	161.9	122.0	135.6	117.3	133.6	161.5	2)
6	43.5	43.8	54.1	55.6	56.3	56.9	116.4	162.7	122.8	135.9	117.6	134.0	160.8	1)
	43.6	43.9	54.3	55.7	56.3	57.1	116.3	162.7	122.9	135.9	117.8	134.1	161.3	2)
7	42.1	48.7	48.7	50.0	53.7	54.0	117.3	163.0	123.0	136.1	117.9	134.0	161.4	1)
	41.6	48.1	48.1	49.3	53.1	53.4	116.3	162.3	122.3	133.5	117.2	133.4	161.6	2)

Solvent and standard: 1) D$_2$O; 2) 1.8 mol dm^{-3} D$_2$SO$_4$, internal dioxane (δ=67.4). a): Atom numbering showed in Fig. 2. [ ]: The chemical shifts could not be assigned to individual carbon.

X-Ray Crystallography of Complex 2. The X-ray structure analysis disclosed that complex **2** comprises [Co(salal)(trien)]$^+$ and Cl$^-$ in 1 : 1 ratio. Since the oxidation state of the cobalt ion is +3, the salicylaldoximato ligand coordinates to the cobalt ion as a dianion form. A perspective view of the complex cation and atom numbering system is shown in Fig. 2. Selected bond distances and angles are listed in Table 6. The complex has a distorted octahedral coordination. The arrangement of the trien ligand about the cobalt center is a *cis*-β configuration. Both of the secondary nitrogen atoms, N(4) and N(7), in the trien ligand take a different chirality (*RS* or *SR*), and five-membered chelate rings adopting the $\delta\lambda\delta$ conformation. The mean Co(III)–N(trien) bond distance (1.949 Å) is almost the same as that (1.951 Å) for a related complex in the *cis*-β_1-(*RS*)-[Co(gly)(trien)]$^{2+}$ cation.[20] However, for Co–N(4) the bond distance (1.889(8) Å) is shorter than the mean value.

The salicylaldoximato ligand is coordinated to the cobalt atom through the N(18) and O(1) atoms. The distances of Co–N(18) and Co–O(1) are 1.935(7) Å and 1.928(6) Å, respectively. These distances are similar to those found in bis(salicylaldoximato)copper(II) (**8**)[15] and bis(salicylaldoximato)palladium(II) (**9**).[16] The C(17)–N(18) bond distance of 1.271(12) Å is comparable to 1.25(2) Å in **8** and 1.291(20) Å in **9**. However, the N(18)–O(2) bond distance of 1.374(9) Å is shorter than those found in **8** and **9** (1.45(2) Å and 1.415(15) Å, respectively). This remarkable shortening may be ascribed to the small participation of the N(18)–O(2) bond into the conjugate π-system. The

Table 5. ^{1}H NMR spectra of Complexes **1**—**7**

	Trien δ					Salicylaldoximato δ		
Complex no.	NH-side methylene protons		NH_2-side methylene protons	NH_2	NH	=CH	Ring protons	Solvent
1	2.48—2.60 (1H) 2.85—3.12 (3H) 3.47—3.62 (1H)	2.76—2.85 (1H) 3.12—3.47 (2H)	2.85—3.12 (2H) 3.12—3.47 (2H)	3.75 (1H) 4.61 (1H) 4.8—5.2 (2H)	5.95 (1H) 6.59 (1H)	8.47 (1H)	6.7—7.4 (4H)	2)
2	2.48—2.57 (1H) 2.88—3.18 (1H)	2.68—2.88 (5H) 3.30—3.42 (1H)	2.88—3.18 (4H)	4.27 (1H) 4.5—6.7 (3H)	5.66 (1H) a)	7.94 (1H)	6.7—7.2 (4H)	1)
	2.60—2.70 (1H) 2.85—3.05 (4H) 3.52—3.65 (1H)	2.70—2.85 (1H) 3.05—3.25 (1H)	3.05—3.25 (4H)	4.70 (2H) 4.90 (1H) 5.05 (1H)	6.19 (1H) 6.78 (1H)	8.34 (1H)	6.7—7.4 (4H)	2)
3	2.70—2.82 (2H) 3.27—3.50 (2H)	2.83—3.04 (2H) 3.50—3.73 (2H)	2.83—3.04 (3H) 3.05—3.24 (1H)	4.70 (1H) 4.83 (2H) 5.05 (1H)	5.78 (1H) 6.37 (1H)	8.28 (1H)	6.7—7.3 (4H)	2)
4	2.30—2.45 (1H) 2.92—3.05 (1H) 3.26—3.41 (1H)	2.67—2.92 (3H) 3.05—3.26 (1H) 3.41—3.52 (1H)	2.67—2.92 (2H) 3.05—3.26 (2H)	3.54 (1H) 4.14 (1H) 4.45 (1H) b)	5.51 (1H) a)	7.98 (1H)	6.7—7.3 (4H)	1)
	2.48—2.62 (1H) 2.85—3.12 (3H) 3.47—3.63 (1H)	2.75—2.85 (1H) 3.12—3.47 (2H)	2.85—3.12 (2H) 3.12—3.47 (2H)	3.83 (1H) 4.48 (1H) 4.96 (2H)	6.07 (1H) 6.39 (1H)	8.41 (1H)	6.7—7.4 (4H)	2)
5	2.55—2.68 (1H) 2.82—3.00 (4H) 3.45—3.59 (1H)	2.68—2.82 (1H) 3.00—3.27 (1H)	3.00—3.27 (4H)	4.75 (1H) b) 5.05 (1H)	6.27 (1H) a)	8.23 (1H)	6.7—7.4 (4H)	1)
	2.60—2.70 (1H) 2.85—3.05 (4H) 3.53—3.65 (1H)	2.70—2.85 (1H) 3.05—3.25 (1H)	3.05—3.25 (4H)	4.72 (2H) 4.90 (1H) 5.05 (1H)	6.20 (1H) 6.80 (1H)	8.34 (1H)	6.7—7.4 (4H)	2)
6	2.60—2.77 (2H) 3.23—3.45 (2H)	2.77—3.06 (2H) 3.55—3.72 (2H)	2.77—3.06 (3H) 3.06—3.23 (1H)	b)	6.42 (1H) a)	8.16 (1H)	6.7—7.3 (4H)	1)
	2.70—2.83 (2H) 3.26—3.50 (2H)	2.83—3.04 (2H) 3.50—3.73 (2H)	2.83—3.04 (3H) 3.05—3.24 (1H)	4.69 (1H) 4.82 (2H) 5.07 (1H)	5.78 (1H) 6.38 (1H)	8.28 (1H)	6.7—7.3 (4H)	2)
7	2.46—2.57 (1H) 2.83—3.08 (3H) 3.45—3.61 (1H)	2.76—2.83 (1H) 3.08—3.45 (2H)	2.83—3.08 (2H) 3.08—3.45 (2H)	3.94 (1H) 4.57 (1H) b) 5.06 (1H)	6.22 (1H) a)	8.40 (1H)	6.7—7.4 (4H)	1)
	2.47—2.62 (1H) 2.85—3.12 (3H) 3.48—3.63 (1H)	2.75—2.85 (1H) 3.12—3.46 (2H)	2.85—3.12 (2H) 3.12—3.47 (2H)	3.83 (1H) 4.44 (1H) 4.96 (2H)	6.06 (1H) 6.44 (1H)	8.41 (1H)	6.7—7.4 (4H)	2)

Solvent and standard: 1) D_2O, 2) 1.8 mol dm^{-3} D_2SO_4, internal DSS ($\delta=0$). a): One proton was exchanged with the solvent proton. b): This signal overlapped with the solvent.

O(2)–N(18)–C(17) bond angle (119.1(7)°) is larger than those (115.0(1.5)° and 114.7°) in **8** and **9**, respectively.

The crystal packing in the unit cell is shown in Fig. 3, and the hydrogen bonding is given in Table 7. The asymmetric unit comprises a cobalt ion, a dianion form of salicylaldoxime, a trien, a chloride ion, a molecule of acetone, and two molecules of water. The oxime oxygen (O(2)) of the salicylaldoximato ligand behaves as an acceptor of two intermolecular hydrogen bonds from the amino group (N(10)–H) of the trien ligand and water molecule. Also, an intramolecular hydrogen bond is observed between the O(2) and the proton on the secondary nitrogen (N(4)–H). The N(4)–H···O(2) distance is 2.651(10) Å. Thus, the mode of binding of the salicy-

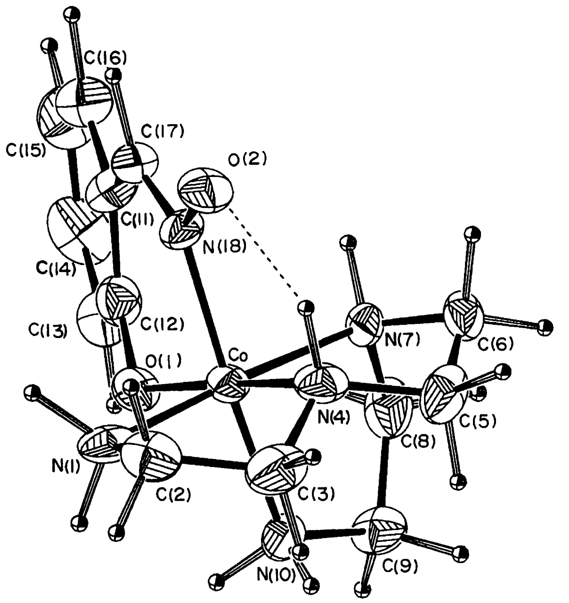

Fig. 2. ORTEP drowing and atom numbering scheme for complex **2**.

Table 6. Selected Bond Distances and Angles of Complex **2**

Bond distances/Å		Bond angles/°	
Co–N(1)	1.933(9)	N(1)–Co–N(4)	86.5(4)
Co–N(4)	1.889(8)	N(1)–Co–N(7)	173.1(3)
Co–N(7)	1.976(7)	N(1)–Co–N(10)	95.3(3)
Co–N(10)	1.999(7)	N(1)–Co–O(1)	93.6(3)
Co–O(1)	1.928(6)	N(1)–Co–N(18)	92.1(3)
Co–N(18)	1.935(7)	N(4)–Co–N(7)	86.7(3)
N(1)–C(2)	1.491(13)	N(4)–Co–N(10)	94.2(3)
C(2)–C(3)	1.469(15)	N(4)–Co–O(1)	177.9(3)
C(3)–N(4)	1.484(14)	N(4)–Co–N(18)	91.2(3)
N(4)–C(5)	1.493(13)	N(7)–Co–N(10)	83.9(3)
C(5)–C(6)	1.496(17)	N(7)–Co–O(1)	93.1(3)
C(6)–N(7)	1.498(12)	N(7)–Co–N(18)	89.3(3)
N(7)–C(8)	1.518(13)	N(10)–Co–O(1)	83.3(3)
C(8)–C(9)	1.538(14)	N(10)–Co–N(18)	171.1(4)
C(9)–N(10)	1.454(13)	O(1)–Co–N(18)	90.9(3)
O(1)–C(12)	1.328(12)	Co–N(4)–O(2)	74.0(3)
O(2)–N(18)	1.374(9)	Co–O(1)–C(12)	123.8(6)
C(17)–N(18)	1.271(12)	N(4)–O(2)–N(18)	78.5(4)
N(4)···O(2)	2.651(10)	Co–N(18)–O(2)	114.5(5)
O(2)···HN(4)	1.89(12)	Co–N(18)–C(17)	126.4(6)
O(2)···HC(17)	2.41(8)	O(2)–N(18)–C(17)	119.1(7)
		N(4)–O(2)–HN(4)	10.4(36)
		N(18)–O(2)–HN(4)	88.8(37)

laldoximato moiety results in a three-point attachment, and the complex ion is able to be stabilized by the formation of a hydrogen bond.21,22)

Isomers of the Complexes. The IR spectra of **1**—**7** show C=N stretching vibrations at 1590—1600 cm^{-1}, which is a very strong band, and have lower wavenumbers than that (1620 cm^{-1}) of free salicylaldoxime; i.e., the azomethin nitrogen of the salicylaldoximato ligand is bonded to a cobalt atom.23,24) Thus, complexes **1**—**7** have been assigned to the **A**- or **B**-types (Fig. 1). A distinction between complexes **1**—**4** and **5**—**7** was found in the electric conductivity, elemental analyses, and preparation. The electric conductivities of **1**—**4** are ca. 120 S cm^2 mol^{-1} in aqueous solutions. The elemental analyses of **1**—**4** agreed with those of $[Co(\mathbf{A})trien]Cl\cdot nH_2O$. On the other hand, the electric conductivities of **5**—**7** are ca. 220 S cm^2 mol^{-1}. The elemental analyses of **5**—**7** agreed with those of $[Co(\mathbf{B})trien]Cl_2$. Complexes **5**, **6**, and **7** were obtained from the reaction mixture of **2**, **3**, and **4** and hydrochloric acid, respectively. Thus, complexes **1**—**4** and **5**—**7** have been assigned to the **A**- and **B**-types, respectively.

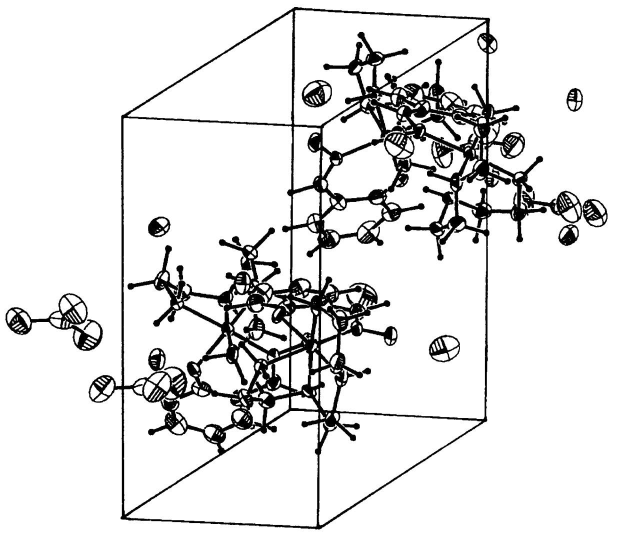

Fig. 3. Molecular arrangement of complex **2** in the unit cell.

Table 7. Hydrogen Bonding and Close Interatomic Distances

Atoms X-H- - -Y	Distances/Å X- - -Y
N(1)-H- - -Cl	3.484(9)
N(4)-H- - -O(2)	2.651(10)a)
N(7)-H- - -OA(1)	2.948(12)
N(10)-H- - -O(2)	2.784(9)
OW(1)-H- - -O(2)	2.596(9)
OW(2)-H- - -OW(1)	2.871(13)
OW(1)-H- - -Cl	3.202(8)
OW(2)-H- - -Cl	3.216(11)

a) Intramolecular hydrogen bond.

Octahedral (salicylaldoximato)(triethylenetetramine)-cobalt(III) complexes exist in three geometrical isomers (*cis*-α, β_1, and β_2),25) and their diastereoisomers (*RR*,*SS* and *RS*,*SR*) arise from asymmetry about the cobalt and secondary nitrogen atoms of trien, as shown in Fig. 4. The IR spectra of **1**—**7** show four or five absorption bands in the NH$_2$ twisting region (990—1100 cm^{-1}, cf. Experimental section). Thus, complexes **1**—**7** are assigned to the *cis*-β-form.1,3—5) A distinc-

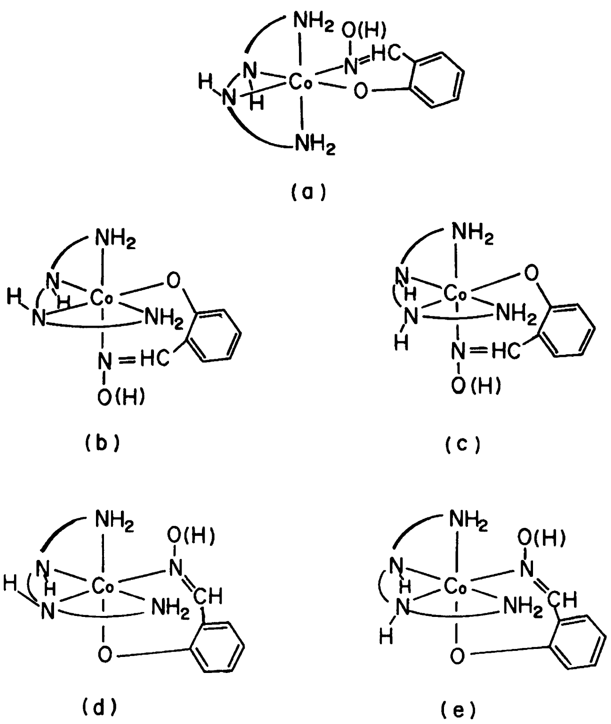

Fig. 4. Various configurational isomers of the (salicylaldoximato)(triethylenetetramine)cobalt(III) complexes: (a) Λ-α-(*RR*), (b) Δ-β_1-(*RR*), (c) Δ-β_1-(*RS*), (d) Δ-β_2-(*RR*), (e) Δ-β_2-(*RS*). Each isomer exists in mirror image forms.

tion between complexes (**1**, **4**) and complexes (**2**, **3**) was observed in the ^{1}H NMR and absorption spectra: The chemical shifts (δ=3.7—3.8) of the proton signal of the NH_2 groups of the coordinated trien ligand of **1** and **4** are at a higher field than those (δ=4.70) of **2** and **3**, i.e., the NH_2 group of **1** and **4** is considered to be at a position trans of the phenoxyl oxygen of the coordinated salicylaldoximato ligand, which is more electronegative than the nitrogen of the oxime group. The ε values of the first absorption bands for **1** and **4** are smaller than those of **2** and **3**. These properties of (**2**, **3**) and (**1**, **4**) are similar to those of the *cis*-β_1 and β_2-(salicylaldehydato)(triethylenetetramine)cobalt(III) chloride hydrates, *cis*-β_1- and β_2-[Co(salad)(trien)]Cl_2·$2H_2O$,[5] respectively. In addition, complex **2** has been confirmed to be the *cis*-β_1 isomer by an X-ray crystallographic analysis (Fig. 2). Thus, complexes (**2**, **3**) and (**1**, **4**) have been assigned to the *cis*-β_1 and β_2 isomers, respectively, as shown in Fig. 4. Complexes **5**, **6**, and **7** were obtained from the reaction mixture of **2**, **3**, and **4** and 2 mol dm^{-3} HCl, respectively. Also, the properties of the NMR and absorption spectra of **5**, **6**, and **7** are similar to those of **2**, **3**, and **4**, respectively. Thus, complexes **5**, **6**, and **7** are assigned to the *cis*-β_1, *cis*-β_1, and *cis*-β_2 isomers, respectively.

cis-β_1 and β_2 Isomers have two diastereoisomers of (*RR*,*SS*) and (*RS*,*SR*) configurations, as shown in Fig. 4. Complex **2** has been confirmed to have the *cis*-β_1-(*RS*,*SR*) configuration based on an X-ray crystallographic analysis (Fig. 2). Complex **3** isomerizes to **2** in an aqueous solution, i.e., complex **3** is assigned to the *cis*-β_1-(*RR*,*SS*) configuration. The absorption spectra of **2** (*RS*,*SR*) and **3** (*RR*,*SS*) have shown two peaks at 355 and 537 nm and three peaks at 350, 470, and 545 nm, respectively. The absorption spectra of **1** and **5** showed two peaks; i.e., complexes **1** and **5** can be assigned to the (*RS*,*SR*) configuration. On the other hand, complexes **4**, **6**, and **7** can be assigned to the (*RR*,*SS*) configuration, because the absorption spectra of **4**, **6**, and **7** showed three peaks. The (*RR*,*SS*) configuration (complex **4**) of the *cis*-β_2 isomer is more stable than the (*RS*,*SR*) configuration of **1**, because **1** isomerizes to **4** in aqueous solution. This property is in agreement with the results of Buckingham et al.,[20,26] i.e., the (*RR*) isomers of *cis*-β_1 and β_2-[Co(gly)(trien)]$^{2+}$ are more stable than (*RS*) isomers, based on the results concerning the relative energies. On the other hand, the (*RR*,*SS*) configuration (complex **3**) of the *cis*-β_1 isomer is less stable than the (*RS*,*SR*) configuration of **2**, because **3** isomerizes to **2**. The stability of **2** is due to an intramolecular hydrogen bond formation between N(4)H and O(2). In the (*RR*,*SS*) configuration (**3**), the hydrogen bond formation is impossible based on the Driding stereo model.

In this study, the **A**- and **B**-type complexes of the mixed-ligand (salicylaldoximato)(triethylenetetramine)cobalt(III) cation were prepared. The different properties between the **A**- and **B**-type complexes are as follows:

i) The yield (26.4%) of the **A**-type complexes was lager than that (5.1%) of the **B**-type complexes.

ii) The CH=N stretching vibrations (ca. 1590 cm^{-1}) in the IR spectra of the **A**-type complexes have a lower wavenumber than those (ca. 1600 cm^{-1}) of **B**-type complexes.

iii) The chemical shifts (δ=148—150) of the C-17 carbon signal in the ^{13}C NMR spectra (D_2O) of the **A**-type complexes are at a higher field than those (δ=160—162) of the **B**-type complexes. In addition, the chemical shifts (δ=120—121) of the C-11 carbon signal are at a lower field than those (δ=116—117) of the **B**-type complexes (Table 4).

iv) The chemical shifts (δ=7.9—8.0) of the CH=N proton signal in the ^{1}H NMR spectra (D_2O) of the **A**-type complexes are at a higher field than those (δ=8.2—8.4) of the **B**-type complexes (Table 5).

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