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Cobalt(III) Complexes with Quadridentate Ligands. X.[1] The Preparation and Properties of Isomers of the Salicylaldehydato(quadridentate amine)cobalt(III) Complexes

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In a recent study, *t*- and *p*-salicylaldehydato[tris(2-aminoethyl)amine]cobalt(III) complexes, *t*- and *p*-$[Co(salad)tren]Cl_2\cdot H_2O$, and *cis*-$\beta_1$- and β_2-*RR,SS*-salicylaldehydato(quadridentate amine)cobalt(III) complexes, *cis*-β_1- and β_2-*RR,SS*-$[Co(salad)L]Cl_2\cdot nH_2O$ (L: 2,3,2-tet; 3,2,3-tet), have been obtained from a reaction mixture of $[CoCl_2L]Cl\cdot nH_2O$ (L: tren; 2,3,2-tet; 3,2,3-tet), Ag_2O, and salicylaldehyde. Two isomers were separated for each complex by SP-Sephadex C-25 column chromatography. The formation ratio of *t*- to *p*-isomers was ca. 1 : 3. The *t*- and *p*-configurations have been established by their absorption and ^1H NMR spectra. On the other hand, the formation ratio of cis-β_1 to β_2-*RR,SS*-isomers was ca. 1 : 1 for both L=2,3,2-tet and 3,2,3-tet ligands. Their configurations have been established by their IR, absorption, and NMR spectra. The corresponding cis-α-isomer could not be obtained. Isomerization between *t*- and *p*-isomers or cis-β_1- and β_2-isomers was not observed in water at room temperature. The formation ratio and the absorption spectra of the complexes are different from those of the corresponding salicylato(quadridentate amine)cobalt(III) chloride hydrate, $[Co(sal)L]Cl\cdot nH_2O$ (L: tren; 2,3,2-tet; 3,2,3-tet), previously reported. These differences have been attributed to a carbonyl bond between the carbonyl oxygen of the formyl group and a cobalt atom in the complexes.

Previously, we were concerned with the preparation and properties of isomers of the *cis*-β-salicylaldehydato(triethylenetetramine)cobalt(III) dichloride dihydrate,[2] *cis*-β-$[Co(salad)trien]Cl_2\cdot 2H_2O$. The corresponding cis-$\alpha$-isomer has not yet been obtained. The formation of the cis-α-isomer might be due to the configurations of the coordinated quadridentate tetramine ligands and to the coordinate atom of the coordinated organo ligands. We selected two ligands of 3,7-diazanonane-1,9-diamine (abbreviation: 2,3,2-tet) and 4,7-diazadecane-1,10-diamine (abbreviation: 3,2,3-tet) which are relatively strain-free[3,4] compared with trien (2,2,2-tet) ligand from their molecular models. On the other hand, the carbonyl oxygen of the formyl group of the salicylaldehydato (formylphenolato) ligand forms a carbonyl bond to a cobalt atom. This property is different from the carbonyl oxygen of the carboxyl group of salicylato and thiosalicylato (*o*-mercaptobenzoato) ligands. Then, *cis*-α-salicylaldehydatocobalt(III) complexes with 2,3,2-tet and 3,2,3-tet ligands may be obtained. Further, the preparation and properties of octahedral salicylaldehydatocobalt(III) complexes with amine ligands have not been studied, except for *cis*-β-$[Co(salad)trien]Cl_2\cdot 2H_2O$, because salicylaldehyde reacts with ammine, *N*-alkyl (or *N*-aryl) amine, ethylenediamine, and quadridentate amine, and yields to the corresponding Schiff base ligands.[5–10] Thus, the present paper deals with the preparation and properties of the mixed-ligand cobalt(III) complexes with salicylaldehydato and tris(2-aminoethyl)amine (abbreviation: tren), 2,3,2-tet or 3,2,3-tet ligands as well as with the assignments of the configurations of these complexes.

Experimental

Measurements. The magnetic susceptibilities were measured by Faraday's method using a magnetic balance (Shimadzu) at room temperature. The electric conductivities in aqueous solutions were determined by the use of a conductometric meter, CM-30 (Shimadzu) at room temperature. The IR spectra were recorded in potassium bromide disks with a 270-30 spectrophotometer (Hitachi). The visible absorption spectra were recorded with a Shimadzu UV-210 recording spectrophotometer. The NMR spectra were recorded with an FX90Q apparatus (JEOL) for ^1H NMR and an FX-60 apparatus (JEOL) for ^{13}C NMR. The melting points were measured on a MP-500D apparatus (Yanako).

Preparation of Complexes. Dichloro[tris(2-aminoethyl)amine]cobalt(III) Chloride Hydrate, $[CoCl_2(tren)]Cl\cdot H_2O$ (1) and *trans*-Dichloro(3,7-diazanonane-1,9-diamine)cobalt(III) Chloride Hydrates, *trans*-$[CoCl_2(2,3,2\text{-}tet)]Cl\cdot 2.5H_2O$ (2), *trans*-Dichloro(4,7-diazadecane-1,10-diamine)cobalt(III) Chloride Hydrate, *trans*-$[CoCl_2(3,2,3\text{-}tet)]Cl\cdot H_2O$ (3): Complexes **1** and **2**, **3** were prepared by the methods of Kimura,[11] and Bosnich,[3,12] respectively.

***t*-Salicylaldehydato[tris(2-aminoethyl)amine]cobalt(III) Dichloride Hydrate (4) and *p*-Salicylaldehydato[tris(2-aminoethyl)amine]cobalt(III) Dichloride Hydrate (5):** Complex **1** (5.0 g, 15.17 mmol) was added to moistened fresh Ag_2O, which was made from silver nitrate (5.17 g, 30.43 mmol) and potassium hydroxide (1.71 g, 30.48 mmol). The mixture was stirred for several minutes at room temperature; then, 10 cm^3 of water was added to the mixture. The mixture was stirred for about 30 min at 60 °C, and the precipitated silver chloride was filtered off and washed with a small amount of water. The methanol solution (20 cm^3) of salicylaldehyde (1.85 g, 15.15 mmol) was added, drop by drop, to the reddish-violet filtrate. The solution was stirred at room temperature for 6 h and was then concentrated on a rotary evaporator and dried. Yield: orange complex (a mixture of **4** and **5**) 3.4 g. The separation of complexes **4** and **5** from the orange complex of 0.5 g was achieved by a column of ion-exchange resin (SP-Sephadex C-25, $\phi 2.5\times 40$ cm). On elution with 0.1 mol dm^{-3} NaCl, the effluent of the first orange band (complex **5**, *p*-isomer) and the second red band (complex **4**, *t*-isomer) was collected and concentrated on a rotary evaporator, and the precipitated NaCl was removed by filtration. Complexes **4** and **5** were recrystallized from methanol-ether. Yields: 0.47 g (7.5%) for **4**, 1.36 g (21.6%) for **5**. Found **4**: C, 37.77; H, 6.23; N, 13.76; Cl, 16.85%. **5**: C, 37.30; H, 6.31; N, 13.73; Cl, 17.34%. Calcd for $CoC_{13}H_{25}N_4O_3Cl_2$ (MW 415.20) C, 37.60; H, 6.07; N, 13.50; Cl, 17.08%. Dp: 188—189 °C for **4**, 191—193 °C for **5**. Λ=245 for **4**, 250 S cm^2 mol^{-1} for **5** in water.

***cis-β*-Salicylaldehydato(3,7-diazanonane-1,9-diamine)-cobalt(III) Dichloride Hydrate:** To a mixture of complex **2** (5.0 g, 13.49 mmol) and Ag_2O (26.96 mmol) was added salicylaldehyde (1.64 g, 13.43 mmol) in methanol (20 cm^3) according to the procedure for complexes **4** and **5**. The solution was stirred at room temperature for 20 h and was then concentrated on a rotary evaporator. The concentrated solution was injected onto an alumina column. Upon elution with methanol, the effluent of the first red band was collected and concentrated. Yield: orange complex (a mixture of **6** and **7**) 3.8 g.

***cis-β*$_1$-Salicylaldehydato(3,7-diazanonane-1,9-diamine)-cobalt(III) Dichloride Dihydrate (6) and *cis-β*$_2$-Salicylaldehydato(3,7-diazanonane-1,9-diamine)cobalt(III) Dichloride Dihydrate (7):** The separation of complexes **6** and **7** from the orange complex of 0.5 g was achieved by a column of ion-exchange resin (SP-Sephadex C-25, $\phi 2.5\times 70$ cm). Upon elution with 0.1 mol dm^{-3} NaCl, the effluents of the upper and lower layers of the orange band were collected and concentrated, respectively. The separated NaCl was removed by filtration. The isolation of complex **6** from the upper layer was achieved by a column of ion-exchange resin by the above method, i.e., the upper layer of orange band was collected again and concentrated. The separated NaCl was removed. Complex **6** was recrystallized from methanol-ether. This procedure was repeated again. The isolation of complex **7** from the lower layer was achieved according to the same procedure for complex **6**. Yields: 0.76 g (12.6%) for **6**, 1.02 g (16.9%) for **7**. Found **6**: C, 37.30; H, 6.41; N, 12.37; Cl, 16.10%. **7**: C, 37.89, H, 6.66; N, 12.25; Cl, 16.08%. Calcd for $CoC_{14}H_{29}N_4O_4Cl_2$ (MW 447.24) C, 37.60; H, 6.54; N, 12.53; Cl, 15.85%. Dp: 201—203 °C for **6**, 206—208 °C for **7**. Λ=225 for **6**, 230 S cm^2 mol^{-1} for **7** in water. IR spectra **6**: 1030, 1045, 1075, 1085 cm^{-1}; 3070, 3100, 3120, 3200 cm^{-1}. **7**: 1030, 1045, 1075, 1085 cm^{-1}; 3060, 3100, 3130, 3200 cm^{-1}.

***cis-β*$_1$-Salicylaldehydato(4,7-diazadecane-1,10-diamine)-cobalt(III) Dichloride Hydrate (8) and *cis-β*$_2$-Salicylaldehydato(4,7-diazadecane-1,10-diamine)cobalt(III) Dichloride Hydrate (9):** A mixture of complexes **8** and **9** was prepared from the reaction mixture of complex **3** (5.0 g, 13.98 mmol), flesh Ag_2O (3.4 g, 14.67 mmol), and salicylaldehyde (1.8 g, 14.74 mmol). Complexes **8** and **9** were isolated according to the method for **6** and **7**, and recrystallized from methanol-ether. Yields: 0.93 g (15.0%) for **8**, 1.26 g (20.3%) for **9**. Found **8**: C, 40.86; H, 6.92; N, 12.40; Cl, 16.16%. **9**: C, 40.96; H, 6.40; N, 12.79; Cl, 16.07%. Calcd for $CoC_{15}H_{29}N_4O_3Cl_2$ (MW 443.26) C, 40.64; H, 6.59; N, 12.64; Cl, 16.00%. Dp: 196—198 °C for **8**, 192—194 °C for **9**. Λ=237 for **8**, 233 S cm^2 mol^{-1} for **9** in water. IR spectra **8**: 1035, 1065, 1080, 1090 cm^{-1}; 3070, 3100, 3120, 3170 cm^{-1}. **9**: 1015, 1040, 1060, 1070 cm^{-1}; 3070, 3100, 3130, 3170 cm^{-1}.

Solubility. All complexes were very soluble in water, methanol, and DMSO, and slightly soluble in ethanol but insoluble in common organic solvents, such as ether and acetone.

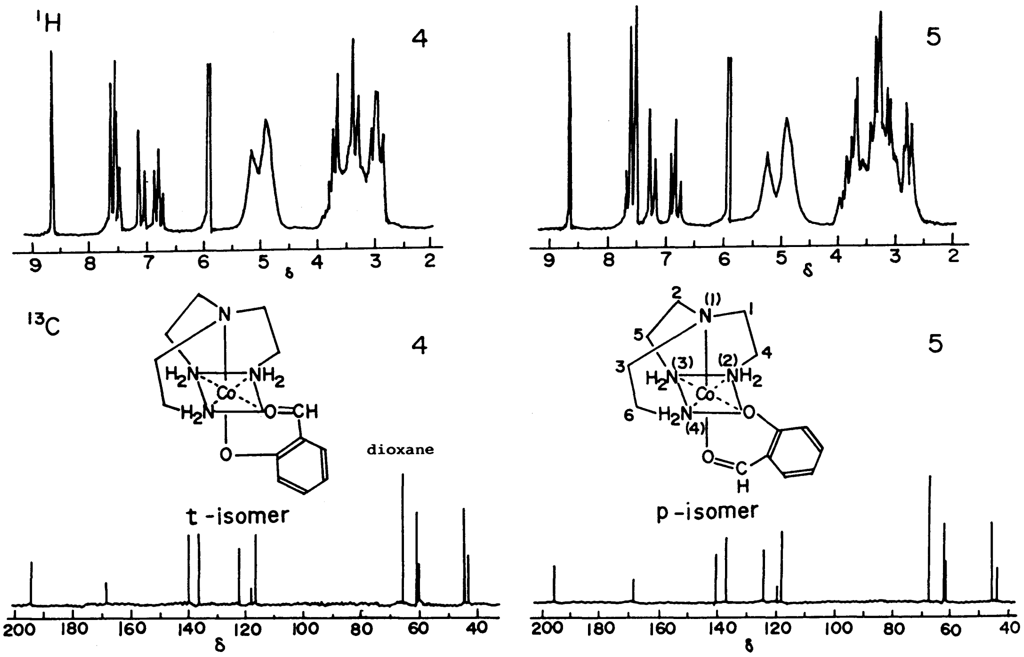


Fig. 1. The *t* and *p* configuration of [Co(salad)tren]$Cl_2\cdot H_2O$, and ^{1}H and ^{13}C NMR spectra of complexes **4** and **5**.

4: *t*-[Co(salad)tren]$Cl_2\cdot H_2O$; **5**: *p*-[Co(salad)tren]$Cl_2\cdot H_2O$. Solvent: ^{1}H NMR, 1.8 mol dm^{-3} D_2SO_4; ^{13}C NMR, D_2O.

Results and Discussion

***t*- and *p*-Salicylaldehydato(tren)cobalt(III) Dichloride Hydrate (*t*: 4, *p*: 5):** Octahedral salicylaldehydato(tren)cobalt(III) complexes exist in two isomeric forms of *t*- and *p*-isomers,[13] as shown in Fig. 1. A mixture of *t*- and *p*-salicylaldehydato(tren)cobalt(III) dichloride hydrate has been obtained from a reaction mixture of $[CoCl_2(tren)]Cl$ (**1**), Ag_2O, and salicylaldehyde. Two geometrical isomers of *t*- (**4**) and *p*- (**5**) of the complex were separated by SP-Sephadex C-25 column chromatography. The formation ratio of **4** to **5** was ca. 1 : 3. The isomerization between **4** and **5** was not observed in water and methanol at room temperature. The electric conductivities for **4** and **5** in aqueous solutions were 245 and 250 $S\,cm^2\,mol^{-1}$, respectively.

The absorption spectra of **4** and **5** were measured in water (Table 1). The absorption bands at around 410 and 500 nm were assigned to a specific absorption band and the first d-d absorption band, respectively.

The ^{13}C NMR spectra of **4** and **5** were measured in D_2O (Fig. 1 and Table 2). Four signals have been observed for the tren ligand and seven signals for the salicylaldehydato ligand. The signals at δ 44.2 and 45.5 for **4** were assigned to the NH_2- side methylene carbons, and those at δ 61.3 and 62.1 were assigned to the -N side methylene carbons.[14] The signals at δ 44.2 and 61.3 were assigned to the C(5) and C(2) carbons, respectively, and those at δ 45.5 and 62.1 were assigned to the C(4), C(6) and C(1), C(3) carbons,[14] respectively. The spectral data of **5** are shown in Table 2.

The ^1H NMR spectra of **4** and **5** were measured in 1.8 $mol\,dm^{-3}$ D_2SO_4 (Fig. 1). The signals of the NH_2- side and -N side methylene protons, ring and formyl group protons of **4** and **5** were assigned by comparisons with those of *t*- and *p*-salicylato(tren)-

Table 1. ^1H NMR and Absorption Spectra of Complexes **4**—**9** and **17**, **18**

^1H Complex No. (isomer)	$N(CH_2CH_2NH_2)_3$ δ NH$_2$- side methylene protons	NH$_2$-+-N side methylene protons	-N side methylene protons	$N(2)H_2+N(3)H_2$
4 (*t*)	2.70—3.13(4H)	3.13—3.95(8H)		4.90(4H)
5 (*p*)	2.55—2.86(2H)	2.86—3.45(6H)	3.45—4.00(4H)	4.80(4H)

x, *y*, *z* (isomer)	$NH_2(CH_2)_xNH(CH_2)_yNH(CH_2)_zNH_2$ δ Center methylene protons	NH_2- side methylene protons	NH- side methylene protons	$N(1)H_2$	$N(4)H_2$	N(3)H
6 2,3,2(β_1)	1.77—2.20(2H)	2.20—3.28(12H)		4.32(2H)	5.12(3H)	
7 2,3,2(β_2)	1.75—2.16(2H)	2.16—2.49(3H)	2.49—3.30(9H)	4.35(1H)4.60(1H)	5.12(3H)	
8 3,2,3(β_1)	1.45—2.26(6H)	2.26—3.22(10H)		3.54(1H)4.28(1H)	4.68(2H)	5.20(1H)
9 3,2,3(β_2)	1.42—2.07(4H)	2.07—2.56(6H)	2.56—3.22(6H)	3.61(1H)4.15—4.90(3H)		5.14(1H)
17 2,2,2(β_1)	—	2.42—3.40(12H)		4.40(2H)	4.98(2H)	6.20(1H)
18 2,2,2(β_2)	—	2.35—2.75(3H)	2.75—3.75(9H)	4.30(1H)4.43—4.92(2H)	5.08(1H)	6.15(1H)

^1H Complex No. (isomer)	$N(CH_2CH_2NH_2)_3$ δ $N(4)H_2$	Salicylaldehydato δ Ring protons	CHO	Absorption bands in water λ/nm ($\varepsilon/cm^{-1}\,mol^{-1}\,dm^3$)
4 (*t*)	5.10(2H)	6.7—7.7(4H)	8.65(1H)	415(2050) 500(235)
5 (*p*)	5.20(2H)	6.7—7.7(4H)	8.63(1H)	405(2100) 490(240)

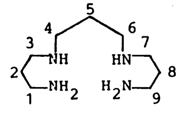
x, *y*, *z* (isomer)	$NH_2(CH_2)_xNH(CH_2)_yNH(CH_2)_zNH_2$ δ N(2)H [N(2)H+Ring protons]	Salicylaldehydato δ Ring protons	CHO	λ/nm ($\varepsilon/cm^{-1}\,mol^{-1}\,dm^3$)
6 2,3,2(β_1)	6.31(1H)	6.6—7.7(4H)	8.54(1H)	412(1900) 500(260)
7 2,3,2(β_2)	6.32(1H)	6.6—7.7(4H)	8.50(1H)	412(1940) 495(240)
8 3,2,3(β_1)	6.23(1H)	6.7—7.8(4H)	8.49(1H)	410(1910) 510(220)
9 3,2,3(β_2)	6.20(1H)	6.6—7.7(4H)	8.60(1H)	410(1980) 505(200)
17 2,2,2(β_1)	[6.5—7.6(5H)]		8.48(1H)	418(2000) 500(292)
18 2,2,2(β_2)	[6.5—7.6(5H)]		8.59(1H)	418(1830) 500(270)

Solvent and standard: 1.8 $mol\,dm^{-3}$ D_2SO_4, internal DSS (δ=0).

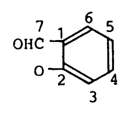
Table 2. ^{13}C NMR Spectra of Complexes 4—9

Complex No.	N($CH_2CH_2NH_2$)$_3$ δ					Salicylaldehydato δ						
	C(5)	C(4) C(6)	C(2)	C(1) C(3)		c-1	c-2	c-3	c-4	c-5	c-6	c-7
4	44.2	45.5	61.3	62.1		120.0	169.5	118.3	141.8	124.1	138.1	196.5
5	43.7	45.5	61.8	62.1		119.7	169.3	118.2	141.3	124.5	137.6	197.0
	$NH_2(CH_2)_xNH(CH_2)_yNH(CH_2)_zNH_2$ δ											
	c-5	c-2 c-8	c-1 c-9	c-3 c-7	c-4 c-6							
6	23.7	— —	[43.2 43.8]	[51.2 55.7]	[46.0 48.0]	120.2	170.2	118.2	141.5	124.2	137.7	196.3
7	23.5	— —	[43.3 43.5]	[51.0 55.7]	[45.2 47.2]	120.1	169.6	118.2	141.3	124.4	137.5	196.4
8	—	[21.6 27.1]	[36.5 38.4]	[44.7 48.3]	[48.3 53.4]	120.4	169.3	118.4	141.6	124.4	137.7	196.1
9	—	[21.8 27.0]	[37.4 38.1]	[45.0 47.7]	[48.5 53.5]	120.3	169.3	118.3	141.3	124.2	137.5	196.0

Solvent and standard: D_2O, internal dioxane (δ=67.4).
[ ]: The chemical shifts could not be assigned to the individual methylene carbon.



Quadridentate amine



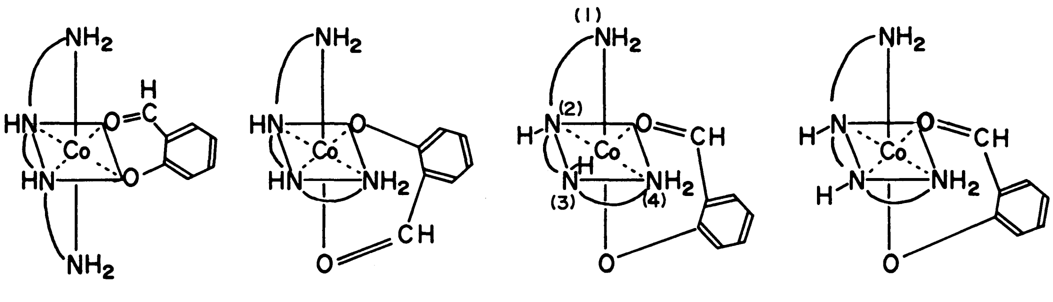
Salicylaldehydato

cobalt(III) chloride hydrate,[14] *t*- and *p*-[Co(sal)-tren]Cl·H_2O (*t*: **10**, *p*: **11**) (Table 1). The amine protons showed two peaks at δ 4.90 and 5.10 for **4** and δ 4.80 and 5.20 for **5** with an intesity ratio of 2:1. The signals at δ 4.90 for **4** and 4.80 for **5** were assigned to N(2)H_2 and N(3)H_2 protons.[14] Those at δ 5.10 for **4** and at δ 5.20 for **5** were assigned to the N(4)H_2 protons.[14]

The chemical shift (δ 4.80) of the proton signal of the NH_2 groups of **5** was at a higher field than that (δ 4.90) of **4**, i.e., the NH_2 group of **5** is considered to be in a position trans to the phenoxyl oxygen of the coordinated salicylaldehydato ligand, which is more electronegative than the formyl oxygen. Also, the methylene proton signals of **5** showed two very sharp peaks[14] in the δ 2.5—2.9 region, but those for **4** did not show the corresponding peaks. In addition, the first absorption band of **4** was at a longer wavelength than that of **5**. These properties of **4** and **5** are in agreement with those of **10** and **11**,[14] respectively. Thus, complexes **4** and **5** have been assigned to *t*- and *p*-isomers, respectively.

The color, melting point, formation ratio, and absorption spectra of **4** and **5** were different from those of **10** and **11**. The color of **4** and **5** was reddish-brown and orange, respectively, but that of **10** and **11** was russet and red, respectively. The melting points (ca. 190 °C) of **4** and **5** were lower than those (ca. 240 °C) of **10** and **11**. The formation ratio of *t*- to *p*-isomers was ca. 1 : 3 for **4** and **5**, but was ca. 3 : 1 for **10** and **11**. The specific absorption bands at around 410 nm of **4** and **5** were at longer wavelengths than those at around 330 nm of **10** and **11**, though the first absorption bands at 490—500 nm for **4** and **5** were at a shorter wavelength than those at 515—530 nm for **10** and **11**. These differences are attributed to a carbonyl bond, i.e., the corbonyl oxygen of the formyl group of **4** and **5** is bonded to a cobalt atom, but the carbonyl oxygen of the carboxyl group of **10** and **11** is not bonded to the cobalt atom.

***cis*-β-Salicylaldehydato(2,3,2-tet)cobalt(III) Dichloride Dihydrate (β₁: 6, β₂: 7) and *cis*-β-Salicylaldehydato-(3,2,3-tet)cobalt(III) Dichloride Hydrate (β₁: 8, β₂: 9):** Octahedral salicylaldehydato(quadridentate amine)-



cis-α cis-β_1 cis-β_2-RR,SS cis-β_2-RS,SR

Fig. 2. The cis-α, β_1, β_2-*RR,SS*, and β_2-*RS,SR* configurations of [Co(salad)(quadridentate amine)]cobalt(III) complexes.

cobalt(III) complexes exist in three geometrical isomers of cis-α, cis-β_1, and cis-β_2. The cis-β-isomers exist in two diastereoisomers of *RR,SS* and *RS,SR*, as shown in Fig. 2. *cis*-β-Salicylaldehydato(quadridentate amine)cobalt(III) dichloride hydrate has been obtained from a reaction mixture of *trans*-[$CoCl_2$-(2,3,2-tet)]Cl·2.5H_2O (**2**) or *trans*-[$CoCl_2$(3,2,3-tet)]-Cl·H_2O (**3**), Ag_2O, and salicylaldehyde. Complexes **6** and **7** or **8** and **9** were separated by SP-Sephadex C-25 column chromatography. Complexes **6**—**9** are highly hygroscopic. Complexes **8** and **9** were diamagnetic from the magnetic susceptibility. The electric conductivities for **6**—**9** in aqueous solutions were 225—237 S cm^2 mol^{-1}.

The absorption spectra of **6**—**9** were measured in water, as shown in Table 1. Their absorption bands at around 410 nm and 500 nm were assigned to the specific absorption band and the first absorption band, respectively.

The ^1H and ^{13}C NMR spectra of **6**—**9** were measured in 1.8 mol dm^{-3} D_2SO_4 and D_2O, respectively. Their center, NH_2- and NH- side methylene protons (and carbons) and salicylaldehydato protons (and carbons) and amine protons were assigned by comparisons with those of *cis*-β-salicylato(quadridentate amine)-cobalt(III) chloride hydrates,[15,16] *cis*-β-[Co(sal)L]Cl·nH_2O (L: trien, β_1: **12**, β_2: **13**; 2,3,2-tet, β_1: **14**, β_2: **15**; 3,2,3-tet, β_2: **16**). Their chemical shifts are shown in Tables 1 and 2. The ^{13}C chemical shifts of the coordinated quadridentate amine ligands were difficult to assign to the individual carbon atoms, but the regions of the chemical shifts of the center, NH_2-, and NH- side methylene carbons were close to those of **12**—**16**.

The IR spectra of **6**—**9** showed four absorption bands in the NH_2 twisting region (990—1100 cm^{-1}) and four absorption bands in the NH stretching region (3000—3300 cm^{-1}). The ^{13}C NMR spectra of **6**—**9** showed 7—8 signals for the quadridentate amine ligand. They indicate that these complexes are assigned to the cis-β-form.[16,17]

A distinction between **6** and **7** was found in the ^1H NMR and absorption spectra. In the ^1H NMR spectra, the methylene proton signals of **6** in the δ 2.2—3.3 region could not be divided into two groups, but those of **7** could be divided into two groups, as shown in Fig. 3. The ε of the first absorption band of **6** was larger than that of **7**, and the band of **6** was at a longer wavelength than that of **7**. These results for **6** and **7** were similar to those of complexes **12**,[15] **14**,[16] and *cis*-β_1-salicylaldehydato(trien)cobalt(III) dichloride dihydrate,[2] *cis*-β_1-[Co(salad)trien]Cl_2·2H_2O (**17**) and complexes **13**,[15] **15**,[16] and *cis*-β_2-[Co(salad)-trien]Cl_2·2H_2O (**18**),[2] respectively. Thus, complexes **6** and **7** were assigned to the cis-β_1 and β_2-isomers, respectively. In complexes **8** and **9**, the ^1H NMR, absorption spectra, and the elution order of the chromatography of **8** and **9** were very close to those of **6**, **17** and **7**, **18**, respectively, i.e., **8** and **9** could be assigned to the cis-β_1 and β_2-isomers, respectively. Next, cis-β-isomer will adopt more stable *RR,SS* configurations; e.g., Buckingham et al. were interested in the stability between the cis-β-*RR,SS* and *RS,SR* configurations of Co(III) complexes with a trien ligand. The *RR,SS* configurations have been shown to be more stable

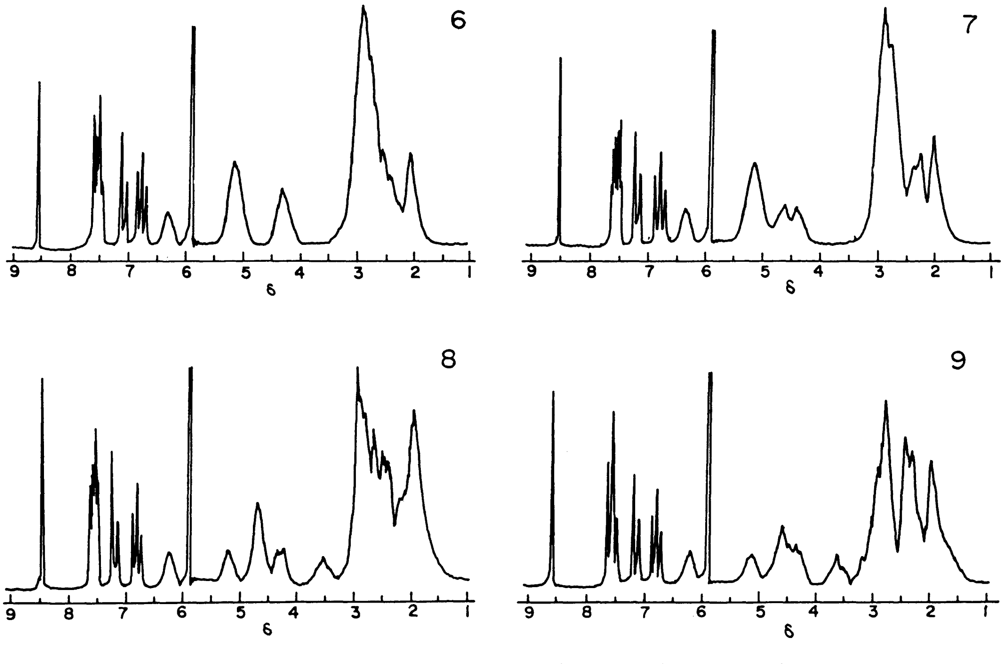


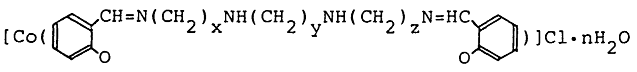
Fig. 3. The ^1H NMR spectra of complexes **6**—**9** in 1.8 mol dm^{-3} D_2SO_4.
6: *cis*-β_1-*RR,SS*-[Co(salad)2,3,2-tet]Cl_2·2H_2O; **7**: *cis*-β_2-*RR,SS*-[Co(salad)2,3,2-tet]-Cl_2·2H_2O; **8**: *cis*-β_1-*RR,SS*-[Co(salad)3,2,3-tet]Cl_2·H_2O; **9**: *cis*-β_2-*RR,SS*-[Co(salad)-3,2,3-tet]Cl_2·H_2O.

than the *RS,SR* configurations for a *cis*-*β*-$[CoL_2(trien)]^{n+}$ (L_2: Cl_2, $(H_2O)_2$, CO_3, gly).[18—20] Also, *cis*-*β*-$[CoL(2,3,2\text{-tet})]^{n+}$ (L: oxalato, glycinato, alaninato, valinato, and sarcosinato),[21,22] *cis*-*β*-$[Co(ox)(Me_2\text{-}2,3,2\text{-tet})]^{+}$,[23] and *cis*-*β*-$[CoL(3,2,3\text{-tet})]^{n+}$ (L: oxalato, acetylacetonato, carbonato)[12,24] have been found to have *RR,SS* configurations by their CD spectra and X-ray diffractions. Thus, we suggest that the structures of **6**—**9** and **17**, **18** are assigned to the *RR,SS* configurations.

The corresponding cis-α isomer has not been obtained in this study and the corresponding studies.[2,15,16,25] However, *cis*-*α*-*RR*,*SS*-$[Co(gly)L]^{2+}$ (gly: $NH_2CH_2COO^-$; L: trien, 3,2,3-tet) has been reported.[22,26] This difference may be due to the coordinate atom of the chelated ligands. Thus, we suggest that the cis-α isomer may be obtained from a reaction mixture of the N-O^- chelate ligand with 2,3,2-tet or 3,2,3-tet ligand.

The color, melting point, and absorption spectra of **6**—**9** and **17**, **18** were different from those of **12**—**16**, such as the corresponding tren complexes. Especially, the cis-$β_1$ of **6**, **8**, and **17** could not be isomerized to the cis-$β_2$ of **7**, **9**, and **18**, respectively, in water, but the cis-$β_1$ of **12** and **14** are isomerized to the cis-$β_2$ of **13** and **15**, respectively,[14] in water at room temperature.

The preparation of the mixed-ligand metal complexes with salicylaldehydato and amine ligands has been difficult, because metal complexes with Schiff base ligands are obtained. In this study, it has been elucidated that the preparation of the mixed-ligand cobalt(III) complexes with salicylaldehydato ligand is dependent upon the reaction temperature. (*N,N'*-Disalicylidene-substituted quadridentate amine)cobalt(III) complexes,[10]



(*x,y,z*: 2,2,2; 2,3,2; 3,2,3; 3,3,3), were prepared from a reaction mixture of $[CoCl_2L]Cl \cdot nH_2O$ (L: quadridentate amine), Ag_2O, and salicylaldehyde in methanol at 50 °C. On the other hand, complexes **6**—**9**, **17**, and **18** were prepared at room temperature from the same reaction mixture.

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