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Cobalt(III) Complexes with Quadridentate Ligands. VII.[1] The Preparation and Properties of the Salicylato or Dichloro[tris-(2-aminoethyl)amine]cobalt(III) Complexes and the Related Complexes

Eiko TOYOTA, Yutaka YAMAMOTO,† and Yoshihisa YAMAMOTO*
Faculty of Pharmaceutical Sciences, Higashi Nippon Gakuen University,
Ishikari-Tobetsu, Hokkaido 061-02
†Tohoku College of Pharmacy, Komatsushima, Sendai 983
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Salicylato- or 3-methyl(or 4-methyl)salicylato[tris(2-aminoethyl)amine]cobalt(III) complexes, [Co(R-sal)tren]Cl·nH$_2$O (R: H, CH$_3$) have been prepared from a reaction mixture of dichloro[tris(2-aminoethyl)amine]cobalt(III) chloride hydrate, [CoCl$_2$(tren)]Cl·H$_2$O, Ag$_2$O, and salicylic acid or 3-methyl- or 4-methylsalicylic acid. Two geometrical isomers (t- and p-) of their complexes were separated by Dowex 50W-X2 column chromatography. Their t- and p-isomers have been established by their ^{1}H NMR and absorption spectra. The formation ratio of t- and p-isomers is ca. 3:1. The isomerization between t-isomer and p-isomer was not observed in water and methanol. In the absorption spectra, the first absorption band for the t- and p-isomers was observed at 535 nm and 515 nm, respectively. In the ^{1}H and ^{13}C NMR spectra of [CoCl$_2$(tren)]Cl·H$_2$O, the signals of the tertiary amine, $-\overset{|}{\underset{|}{N}}-$, side methylene protons and methylene carbons have been assigned to the individual methylene protons and methylene carbons of the coordinated tris(2-aminoethyl)amine ligand.

In this series, the previous papers[1,2] have been concerned with the preparation, properties, and NMR spectra of isomers such as the *cis*-β_1, β_2-salicylato- or salicylaldehydato(triethylenetetramine)cobalt(III) chloride hydrates. In the NMR spectra, the signals for center, NH$_2$- side, -NH- side, and =N- side methylene protons and carbons for the cobalt(III) complexes with quadridentate amine ligands have been assigned.[3,4] The signals for $-\overset{|}{\underset{|}{N}}-$ side methylene protons and carbons have, however, so far remained unsolved. Octahedral cobalt(III) complexes with a tris(2-aminoethyl)amine (abbreviation: tren) ligand are suitable for NMR studies. In addition, the coordinated tren ligand to a metal ion has a tripodal-type configuration, and is different from a linear-type configuration such as trien ligand. We are therefore interested in the difference between tren and trien complexes. Many tren cobalt(III) complexes have been reported with such aliphatic compounds as NH$_2$CH$_2$COOH,[5] CH$_3$SCH(CH$_3$)COOH,[6] CH$_3$SCH$_2$CH$_2$NH$_2$,[7] CH$_3$SeCH$_2$CH$_2$NH$_2$,[8] and their related compounds;[9,10] however, little is known about the preparation and properties of tren cobalt(III) complexes with the organic ligands such as salicylic acid,[2,3] salicylaldehyde,[1] 8-quinolinol,[11] and their related compounds.[12]

The present paper deals with the preparation and properties of t- and p-salicylato or 3-methyl(or 4-methyl)salicylato(tren)cobalt(III) complexes, [Co(R-sal)tren]Cl·nH$_2$O (R: H, CH$_3$); it deals with the assignments of the configuration of t- and p-isomers,[13] and of ^{1}H and ^{13}C chemical shifts of the $-\overset{|}{\underset{|}{N}}-$ side methylene protons and carbons for [CoCl$_2$(tren)]-Cl·H$_2$O and [Co(R-sal)tren]Cl·nH$_2$O (R: H, CH$_3$).

Experimental

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

Preparation of Complexes. Dichloro[tris(2-aminoethyl)-amine]cobalt(III) Chloride Hydrate (1): This complex was prepared by the method of Kimura et al.[9]

Mixture of t- and p-Salicylato[tris(2-aminoethyl)-cobalt(III) Chloride Dihydrate: Complex **1** (10.0 g, 30.3 mmol) was added to moistend fresh Ag$_2$O, which was made from silver nitrate (10.4 g, 61.2 mmol) and potassium hydroxide (3.44 g, 61.3 mmol). The mixture was stirred for several minutes at room temperature, then 20 cm^3 of water was added to the mixture. The mixture was stirred for about 30 min at 60 °C. Thus the precipitated silver chloride was filtered off and washed with a small amount of water. To the reddish violet filtrate was added 4.2 g (30.4 mmol) of salicylic acid. The solution was stirred at 50 °C for 24 h, and concentrated on a rotary evaporator. The concentrated solution was injected into a column chromatograph on alumina. Upon elution with methanol–ethanol (1:1), the first reddish violet band was collected and concentrated on a rotary evaporator. Yield: 3.4 g (27.2%).

Separation of t-Salicylato[tris(2-aminoethyl)amine]cobalt-(III) Chloride Dihydrate (2) and p-Salicylato[tris(2-amino-ethyl)amine]cobalt(III) Chloride Dihydrate (3): The separation of complexes **2** and **3** from the mixture complex of 0.5 g was achieved by a column of ion-exchange resin (Dowex

50W-X2, Na^+ form, ϕ2.5×25 cm). Upon elution with 0.4 mol dm^{-3} NaCl, the effluent of the first reddish violet band (*t*-isomer) and that of the second red band (*p*-isomer) was collected and concentrated, respectively. The separated NaCl was removed. The purification for the *t*- and *p*-isomers was recrystallized from methanol-ether, respectively. Color: russet for **2**, red for **3**. Yields: 2.15 g (17.2%) for **2**, 0.8 g (6.4%) for **3**. Found **2**: C, 38.02; H, 6.51; N, 13.74; Cl, 8.88%. **3**: C, 38.11; H, 6.16; N, 13.71; Cl, 8.87%. Calcd for $CoC_{13}H_{26}N_4O_5Cl$ (MW 412.76) C, 37.83; H, 6.35; N, 13.57; Cl, 8.59%. Mp: 240 °C for **2**, 242 °C for **3**. Λ=130 for **2** and 110 S cm^2 mol^{-1} for **3** in water.

***t*-3-Methylsalicylato[tris(2-aminoethyl)amine]cobalt(III) Chloride Hydrate (4) and *p*-3-Methylsalicylato[tris(2-aminoethyl)amine]cobalt(III) Chloride Hydrate (5):** A mixture of complexes **4** and **5** has been prepared from a reaction mixture of **1** (10.0 g, 30.3 mmol), Ag_2O (7.02 g, 30.3 mmol) and 3-methylsalicylic acid (4.6 g, 30.2 mmol) according to the method used for complexes **2** and **3**. A separation for complexes **4** and **5** was achieved by using a column of ion-exchange resin (Dowex 50W-X2, Na^+ form, ϕ2.5×25 cm). Upon ellution with 0.2 mol dm^{-3} NaCl, the effluent of the first reddish violet band (complex **4**) and the second red band (complex **5**) was collected and concentrated on a rotary evaporator, respectively. The precipitated NaCl was removed by filtration. The purification for the *t*- and *p*-isomers was recrystallized from methanol-ether. Color: russet for **4**, red for **5**. Yields: 1.86 g (15.0%) for **4**, 0.58 g (4.7%) for **5**. Found **4**: C, 40.88; H, 6.52; N, 13.54; Cl, 8.91%. **5**: C, 40.92; H, 6.61; N, 13.84; Cl, 8.97%. Calcd for $CoC_{14}H_{26}N_4O_4Cl$ (MW 408.77) C, 41.14; H, 6.41; N, 13.71; Cl, 8.67%. Mp: 244 °C for **4**, 246 °C for **5**. Λ=125 for **4** and 113 S cm^2 mol^{-1} for **5** in water.

***t*-4-Methylsalicylato[tris(2-aminoethyl)amine]cobalt(III) Chloride Hydrate (6) and *p*-4-Methylsalicylato[tris(2-aminoethyl)amine]cobalt(III) Chloride Hydrate (7):** The preparation and separation for complexes **6** and **7** are attempted using the method for complexes **4** and **5**. Color: russet for **6**, red for **7**. Yields: 2.04 g (16.5%) for **6**, 0.45 g (3.6%) for **7**. Found **6**: C, 40.95; H, 6.62; N, 13.81; Cl, 8.82%. **7**: C, 40.85; H, 6.59; N, 13.66; Cl, 8.89%. Calcd for $CoC_{14}H_{26}N_4O_4Cl$ (MW 408.77) C, 41.14; H, 6.41; N, 13.71; Cl, 8.67%. Mp: 248 °C for **6**, 249 °C for **7**. Λ=115 for **6** and 110 S cm^2 mol^{-1} for **7** in water.

***t*-Salicylato[tris(2-aminoethyl)amine]cobalt(III) Nitrate Hydrate (8) and *p*-Salicylato[tris(2-aminoethyl)amine]cobalt(III) Nitrate (9):** Complexes **8** and **9** were prepared from the reaction mixture of silver nitrate (0.21 g, 1.24 mmol) and **2** or **3** (0.5 g, 1.21 mmol), respectively. They were recrystallized from methanol-acetone. Color: russet for **8**, red for **9**. Yields: 0.34 g (66.7%) for **8**, 0.36 g (73.8%) for **9**. Found **8**: C, 37.06; H, 6.02; N, 16.88%. Calcd for $CoC_{13}H_{24}N_5O_7$ (MW 421.30) C, 37.06; H, 5.74; N, 16.62%. Found **9**: C, 38.73; H, 5.45; N, 17.11%. Calcd for $CoC_{13}H_{22}N_5O_6$ (MW 403.29) C, 38.72; H, 5.50; N, 17.37%. Mp: 237 °C for **8**, 243 °C for **9**. Λ=106 for **8** and 114 S cm^2 mol^{-1} for **9** in water.

Solubility. Complexes **2**—**9** are very soluble in water and DMSO, and soluble in methanol but insoluble in the other common organic solvents such as acetone, ether, and benzene.

Results and Discussion

Dichloro[tris(2-aminoethyl)amine]cobalt(III) Chloride Hydrate (1): The ^1H NMR spectrum of **1** was measured in 1.8 mol dm^{-3} D_2SO_4. The signals at δ 2.5—3.9 and δ 4.6—5.7 of **1** were assigned to the methylene and amine protons of the coordinated tren ligand, respectively. The methylene protons of the coordinated tren ligand showed two signals at δ 2.50—3.03 (4H) and 3.03—3.90 (8H), as shown in Fig. 1. The signals at δ 2.50—3.03 at the highest field are assigned to the NH_2- side methylene protons[3] of the tren ligand. The signals at δ 3.03—3.90 have been assigned to the tertiary amine, $-\overset{|}{\underset{|}{N}}-$, side methylene protons. Two protons of the NH_2- side methylene protons at δ 2.50—3.03 overlapped with the $-\overset{|}{\underset{|}{N}}-$ side methylene protons of the tren ligand; this might be due to the electronic effect of the N(3)H_2 group, which is in a trans position for the Cl(1) ligand. Then, the

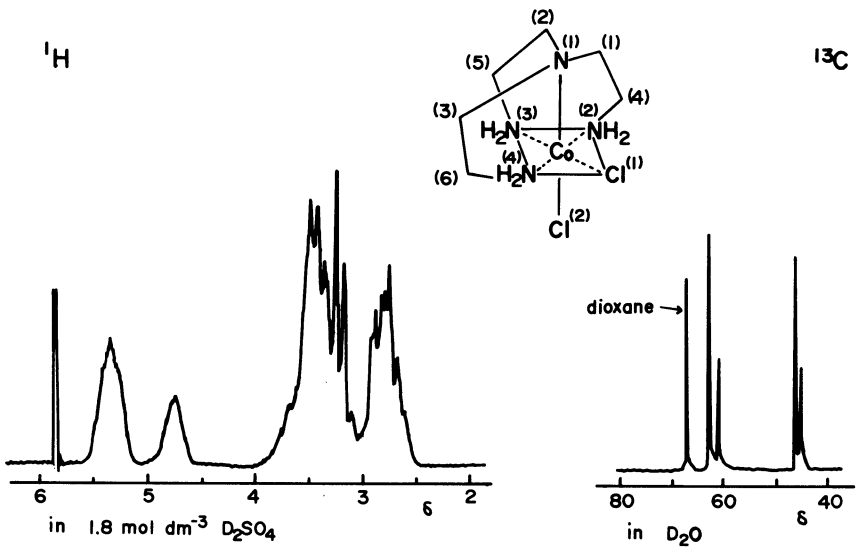


Fig. 1. The ^1H and ^{13}C NMR spectra of $[CoCl_2(tren)]Cl \cdot H_2O$.

methylene proton signals at δ 2.50—3.03 can be assigned to C(4)H_2 and C(6)H_2 protons, and those at δ 3.03—3.90 can be assigned to C(1)H_2, C(2)H_2, C(3)H_2, and C(5)H_2 protons.

The amine protons of the coordinated tren ligand showed two signals at δ 4.78 (2H) and 5.37 (4H), as shown in Fig. 1. The signal at δ 4.78 is assigned to the N(3)H_2 protons of the tren ligand in a position trans to the Cl(1) ligand. The signal at δ 5.37 is assigned to the N(2)H_2 and N(4)H_2 protons of the tren ligand in a position cis to the Cl(1) ligand. The above assignments were made in view of the following: studies of pentaammine(aniono)cobalt(III) ions, $[CoX(NH_3)_5]^{n+}$ (X: Cl, Br, OH···), have been reported by Buckingham,[14] Jolly,[15] Clifton,[16] who described that the chemical shift of the NH_3 group in a position trans to the electronegative atom (X) is at higher fields than those of NH_3 groups in a position cis to the electronegative atom.

The ^{13}C NMR spectrum of **1** was measured in D_2O. Both the signals at δ 45.4 and 46.6 are assigned to the NH_2- side methylene carbons[3] of the tren ligand, as shown in Fig. 1. The signals at δ 61.2 and 63.0 have been assigned to the –N< side methylene carbons. The methylene carbon signals at δ 45.4 and 61.2 are assigned to the C(5)H_2 and C(2)H_2 carbon, respectively, since both carbons are in a trans position for the Cl(1) ligand, and both carbon signals are smaller than those at δ 46.6 and 63.0. The signals at δ 46.6 and 63.0 are assigned to the C(4)H_2, C(6)H_2 and C(1)H_2, C(3)H_2, respectively.

Salicylato- or 3-Methyl(or 4-methyl)salicylato(tren)-cobalt(III) Chloride Hydrates (2—7): The abbreviations of the salicylato or 3-methyl(or 4-methyl)salicylato(tren)cobalt(III) complexes studied in this paper are listed in Table 1. The title complexes have *t*- and *p*-isomers, as shown in Fig. 2. A mixture of *t*- and *p*-salicylato(tren)cobalt(III) chloride dihydrate (**2**, **3**) or *t*- and *p*-3-methyl(or 4-methyl)salicylato(tren)-cobalt(III) chloride hydrate (**4**—**7**) has been isolated from a reaction mixture of complex **1**, Ag_2O, and salicylic acid or 3-methyl(or 4-methyl)salicylic acid. The separation of *t*- and *p*-isomers was attempted using an ion-exchange resin. The formation ratio of *t*- and *p*-isomers was ca. 3:1. The isomerization between *t*- and *p*-isomers is not observed in water and methanol. The corresponding nitrates (**8**, **9**) were prepared from the reaction mixture of complex **2** or **3** and silver nitrate, respectively. Complexes **2** and **3** were diamagnetic from the magnetic susceptibility. The electric conductivities for **2**—**9** in aqueous solutions were 106—130 S cm^2 mol^{-1}.

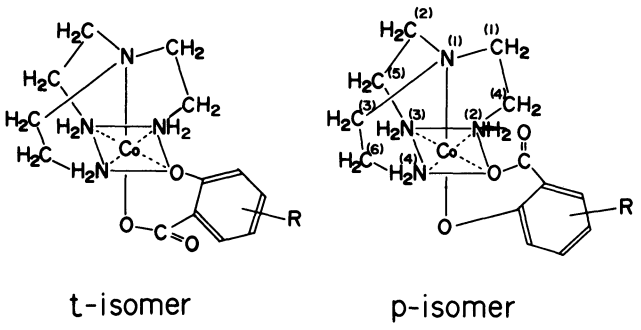


Fig. 2. Two geometrical isomers of [Co(R-sal)tren]-Cl·nH_2O (R: H, CH_3).

In the ^1H NMR spectra, the signals at δ 2.5—4.0 and 4.6—5.3 of **2** and **3** were assigned to the methylene protons and the amine protons of the coordinated tren ligand, respectively, and the lowest field signals at δ 6.5—8.0 were assigned to the coordinated salicylato protons.[17] The methylene proton signals for the tren ligand in **2** are divided into two groups at the δ 2.6—3.1 and 3.1—4.0 regions. On the other hand, those for **3** are divided into three groups at the δ 2.5—2.8, 2.8—3.4, and 3.4—4.0 regions, as shown in Fig. 3. The methylene proton signals at δ 2.6—3.1 for **2** and at δ 2.5—2.8 for **3** are assigned to the NH_2- side methylene protons,[2,3] and those at δ 3.4—4.0 for **3** have been assigned to the –N< side methylene protons as shown in Table 2.

The amine protons for **2** showed one peak at δ 5.00, though those for **3** showed two peaks at δ 4.85 and 5.10 with an intensity ratio 2:1 as shown in Fig. 3. The signal at δ 4.85 of **3** is assigned to N(2)H_2 and N(3)H_2 protons, and that at δ 5.10 is assigned to the N(4)H_2 protons. The chemical shift (δ 4.85) of the proton signal of the NH_2 groups of **3** is at a higher field than that (δ 5.10) of **2**, i.e., the NH_2 group of **3** is considered to be at a position trans to the carboxyl oxygen of the coordinated salicylato ligand, which is more electronegative than the phenoxyl oxygen.[2,17] Thus, complexes **2** and **3** have been assigned to the *t*- and *p*-isomers, respectively. Also, the signals of the

Table 1. The Abbreviations of the (Methyl)salicylato(tren)cobalt(III) Complexes

$[Co(^{OOC}_{O}\!\!\langle\!\!\rangle\!\!-R)tren]X\cdot nH_2O$

No.	2	3	4	5	6	7	8	9
Form	*t*	*p*	*t*	*p*	*t*	*p*	*t*	*p*
R	H	H	3-Me	3-Me	4-Me	4-Me	H	H
X	Cl	Cl	Cl	Cl	Cl	Cl	NO_3	NO_3
n	2	2	1	1	1	1	1	0

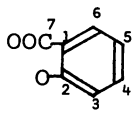
Table 2. ^1H and ^{13}C NMR Spectra of Complexes **2**—**9**

^1H Complex No. (isomer)	Tren δ			
	NH_2- side methylene protons	NH_2-+-N side methylene protons	-N side methylene protons	$N(3)H_2$ $N(2)H_2$ $N(4)H_2$
2 (*t*)	2.60—3.10(4H)	3.10—3.90(8H)		5.00(6H)
3 (*p*)	2.50—2.80(2H)	2.80—3.45(6H)	3.45—3.93(4H)	4.85(4H) 5.10(2H)
4 (*t*)	2.68—3.13(4H)	3.13—3.90(8H)		4.80(2H) 5.00(4H)
5 (*p*)	2.55—2.86(2H)	2.86—3.50(6H)	3.50—4.00(4H)	4.82(4H) 5.10(2H)
6 (*t*)	2.65—3.10(4H)	3.10—3.85(8H)		4.98(6H)
7 (*p*)	2.50—2.80(2H)	2.80—3.45(6H)	3.45—3.92(4H)	4.80(4H) 5.07(2H)
8 (*t*)	2.66—3.11(4H)	3.11—3.86(8H)		4.93(6H)
9 (*p*)	2.50—2.80(2H)	2.80—3.43(6H)	3.43—3.98(4H)	4.80(4H) 5.05(2H)

^1H Complex No. (isomer)	(Methyl)salicylato δ		Absorption band λ/nm (ε/cm^{-1} mol^{-1} dm^3)	
	ring protons	CH_3		
2 (*t*)	6.6—8.0(4H)	—	330(3000)	535(225)
3 (*p*)	6.6—7.9(4H)	—	332(3000)	515(210)
4 (*t*)	6.5—7.8(3H)	2.22(3H)	332(3200)	545(270)
5 (*p*)	6.5—7.8(3H)	2.34(3H)	335(3400)	515(230)
6 (*t*)	6.5—7.9(3H)	2.27(3H)	327(3300)	535(240)
7 (*p*)	6.5—7.8(3H)	2.30(3H)	330(3100)	515(220)
8 (*t*)	6.6—7.9(4H)	—	330(3000)	535(225)
9 (*p*)	6.5—7.9(4H)	—	332(3000)	515(210)

^{13}C Complex No.	Tren δ			
	NH_2- side methylene carbons		-N side methylene carbons	
	C(5)	[C(4), C(6)]	C(2)	[C(1), C(3)]
2	44.0	[45.4]	60.7	[61.4]
3	43.4	[45.2]	61.2	[61.5]
8	43.9	[45.4]	60.7	[61.3]
9	43.5	[45.4]	61.3	[61.6]

^{13}C Complex No.



δ

	C-1	C-2	C-3	C-4	C-5	C-6	C-7
2	118.8	167.9	117.3	134.6	123.6	132.6	174.0
3	117.4	167.7	117.0	134.6	124.7	132.4	174.6
8	118.7	167.9	117.3	134.6	123.6	132.6	174.0
9	117.5	167.7	117.0	134.6	124.8	132.5	174.6

Solvent and Standard: ^1H NMR spectra; 1.8 mol dm^{-3} D_2SO_4, internal DSS (δ=0), ^{13}C NMR spectra; D_2O, internal dioxane (δ=67.4), Absorption spectra; H_2O.

methylene protons of **3** are complicated signals compared with those of **2**. This can be due to the magnetic anisotropy between carbonyl oxygen of the coordinated salicylato ligand and methylene protons of the tren ligand, i.e., molecular models indicate that the carbonyl oxygen of the *p*-isomer has very near position for the methylene protons of the tren ligand, though that of the *t*-isomer has no such methylene protons around the carbonyl group. Also, the methylene protons for **3** showed two very sharp peaks in the δ 2.5—2.8 region, but those for **2** did not show the corresponding peaks. Thus, complexes **2** and **3** are assigned to the *t*- and *p*-isomers, respectively. In addition, a distinction between *t*- and *p*-isomers was found in the amine proton signals for **4** and **5**. The amine proton signal of **4** is different from those for **2** and **6**, but that for **5** is similar to those of **3** and **7** as shown in Fig. 3. This difference is attributed to the

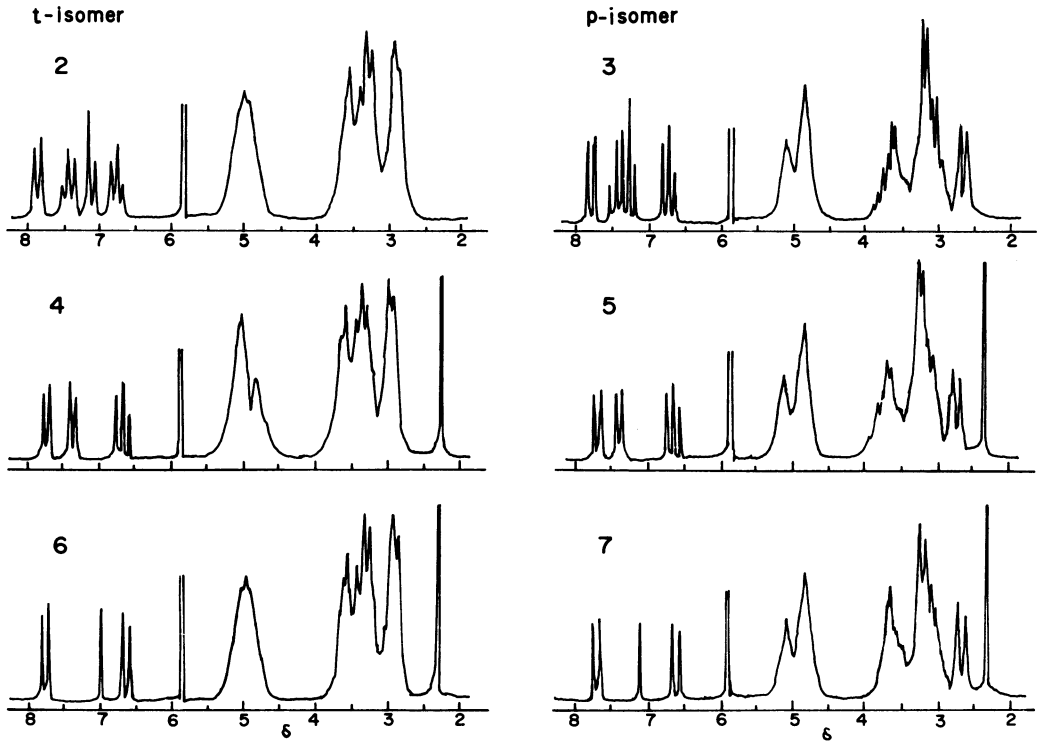


Fig. 3. The ^1H NMR spectra of complexes **2**—**7** in 1.8 mol dm^{-3} D_2SO_4.
2: *t*-[Co(sal)tren]Cl·$2H_2O$; **3**: *p*-[Co(sal)tren]Cl·$2H_2O$; **4**: *t*-[Co(3-Mesal)tren]Cl·H_2O; **5**: *p*-[Co(3-Mesal)tren]Cl·H_2O; **6**: *t*-[Co(4-Mesal)tren]Cl·H_2O; **7**: *p*-[Co(4-Mesal)tren]Cl·H_2O.

methyl group of the coordinated 3-methylsalicylato ligand. The methyl group of the 3-methylsalicylato ligand of **4** has the electronic effect to the phenoxyl oxygen, and the electronic state on the oxygen is a more electronegative, i.e., the amine protons split into two peaks. Accordingly, the $N(3)H_2$ group of **4** is considered to be at a position trans to the phenoxyl oxygen of the 3-methylsalicylato ligand. On the other hand, the $N(3)H_2$ group of **5** is considered to be at a position trans to the carboxyl oxygen from the results of the amine proton signals between **5** and **3**, **7**. Thus, complexes **4** and **5** have been assigned to the *t*- and *p*-isomers, respectively.

In the ^{13}C NMR spectra of complexes **2** and **3** in D_2O, there have been observed four signals for the coordinated tren ligand and seven signals for the coordinated salicylato ligand. The signals at δ 44.0, 45.4 for **2** are assigned to the NH_2- side methylene carbons. The signals at δ 60.7 and 61.4 for **2** have been assigned to the $-\overset{|}{\underset{|}{N}}$ side methylene carbons. The signals at δ 44.0 and 60.7 of **2** are assigned to the C(5) carbon and C(2) carbon, respectively, since both carbons are in the trans position for the phenoxyl oxygen, and their signals are smaller than those at δ 45.4 and 61.4. The signals at δ 45.4 and 61.4 are assigned to the C(4), C(6) and C(1), C(3) carbons, respectively. The distinction for *t*- and *p*-isomers is difficult from the results of the ^{13}C NMR spectra. The results of **3**, **8**, and **9** are collected in Table 2.

In the absorption spectra of complexes **2**—**7**, the absorption bands at ca. 330 nm for **2**—**7** were assigned to the specific absorption band.[3] The absorption bands at ca. 535 nm for **2**, **4**, and **6**, and those at 515 nm for **3**, **5**, and **7** were assigned to the first d–d absorption band ($^1T_{1g} \leftarrow {}^1A_{1g}$).[1] The first absorption bands of **2**, **4**, and **6** are at a longer wavelength than those of **3**, **5**, and **7**, respectively. This difference is agreement with that of the corresponding *cis*-β_1, β_2-salicylato- or 3-methyl(or 4-methyl)salicylato(trien)cobalt(III) complexes,[2,12] *cis*-β_1, β_2-[Co(R-sal)trien]Cl·nH_2O (R=H: β_1(**10**), β_2(**11**); R=3-CH_3: β_1(**12**), β_2(**13**); R=4-CH_3: β_1(**14**), β_2(**15**)). Thus, the NH_2 group of **3**, **5**, and **7** can be also considered to be at a position trans to the carboxyl oxygen of the coordinated salicylato ligand such as the *cis*-β_2 trien complexes (**11**, **13**, **15**). Also, the first absorption band (515 nm) of **5** is similar to those (515 nm) for **3** and **7**, but that (545 nm) of **4** is different from those (535 nm) for **2** and **6**, as is shown in Table 2. This can be due to the electronic effect of the methyl group of the coordinated 3-methylsalicylato ligand in complex **4** as previously described. Thus, complexes **2**, **4**, **6** and complexes **3**, **5**, **7** are assigned to *t*- and *p*-isomers, respectively.

The melting points, visible absorption spectra, colors of the solid state and solubilities of **2** and **3** are

almost similar to those of the trien complexes **10** and **11**. On the other hand, the isomerization between **2** and **3** is not observed, but complex **10** isomerizes to **11** in water at room temperature.

Some properties for complexes **2—9** are collected in Table 2 and the Experimental section.

References

1) Part VI: Y. Yamamoto, E. Toyota, and S. Tsukuda, *Bull. Chem. Soc. Jpn.*, **58**, 1595 (1985).
2) Y. Yamamoto and E. Toyota, *Bull. Chem. Soc. Jpn.*, **52**, 2540 (1979).
3) Y. Yamamoto, H. Kudo, and E. Toyota, *Bull. Chem. Soc. Jpn.*, **56**, 1051 (1983).
4) Y. Yamamoto and S. Tsukuda, *Bull. Chem. Soc. Jpn.*, **58**, 1509 (1985).
5) Y. Mitsui, J. Watanabe, Y. Harada, T. Sakamaki, Y. Iitaka, Y. Kushi, and E. Kimura, *J. Chem. Soc., Dalton Trans.*, **1976**, 2095.
6) M. Kojima and J. Fujita, *Bull. Chem. Soc. Jpn.*, **56**, 2958 (1983).
7) W. G. Jackson and A. M. Sargeson, *Inorg. Chem.*, **17**, 2165 (1978).
8) K. Nakajima, M. Kojima, and J. Fujita, *Chem. Lett.*, **1982**, 925.
9) E. Kimura, S. Young, and J. P. Collman, *Inorg. Chem.*, **9**, 1183 (1970).
10) M. Kojima and J. Fujita, *Bull. Chem. Soc. Jpn.*, **56**, 139 (1983).
11) Y. Yamamoto, E. Toyota, and Y. Yamamoto, *Bull. Chem. Soc. Jpn.*, **56**, 2721 (1983).
12) Y. Yamamoto, E. Toyota, and N. Mitsudera, *Bull. Chem. Soc. Jpn.*, **53**, 3517 (1980).
13) The designations *t* and *p* refer to the position of the carboxyl oxygen trans to a tertiary (*t*) or a primary (*p*) amine nitrogens of tren, respectively.
14) D. A. Buckingham, I. Olsen, and A. M. Sargeson, *Aust. J. Chem.*, **20**, 597 (1967).
15) W. L. Jolly, A. D. Jarris, and T. S. Briggs, *Inorg. Chem.*, **4**, 1064 (1965).
16) P. Clifton and L. Pratt, *Proc. Chem. Soc.*, **1963**, 339.
17) Y. Yamamoto, *Bull. Chem. Soc. Jpn.*, **51**, 2894 (1978).