724 © 1989 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 62, 724—729 (1989) [Vol. 62, No. 3

Cobalt(III) Complexes with Quadridentate Ligands. VIII.[1] The Preparation and Properties of Cis-β_1 and β_2-Isomers of the Thiosalicylato(quadridentate amine)cobalt(III) Complexes

Yoshihisa YAMAMOTO,* Kayoko YOSHII, Eiko TOYOTA, and Kazuko KONNO
Faculty of Pharmaceutical Sciences, Higashi Nippon Gakuen University,
Ishikari-Tobetsu, Hokkaido 061-02

(Received May 2, 1988)

cis-β_1 and β_2-Thiosalicylato(quadridentate amine)cobalt(III) complexes, *cis*-β_1, β_2-[Co(thiosal)L]X·nH$_2$O (L: trien (2,2,2-tet), 3,2,3-tet; X: Cl, NO$_3$), have been prepared from a reaction mixture of [CoCl$_2$L]Cl·nH$_2$O (L: trien, 3,2,3-tet), Ag$_2$O, thiosalicylic acid (*o*-mercaptobenzoic acid), and 28% aqueous ammonia. Two geometrical isomers (cis-β_1 and β_2) of their complexes were separated by Dowex 50W-X2 column chromatography. The isomerization between the cis-β_1 and β_2-isomers is reversible in water at 40 °C. The IR spectra of these complexes showed four or five absorption bands in the 990—1100 cm^{-1} region and four absorption bands in the 3000—3300 cm^{-1} region. This indicates that these complexes assume the cis-β-form. Their cis-β_1 and β_2 configurations have been established by their absorption and NMR spectra. The *cis*-β_1 and β_2-thiosalicylato(trien)cobalt(III) complexes have been tentatively assigned to the *RR,SS* diastereoisomer by their ^{1}H NMR spectra. The color of solid state materials, solubilities in alcohols, isomerization at 40 °C, reaction in 60% nitric acid, absorption spectra, and chemical shift of Co–S–C carbon of the coordinated thiosalicylato ligand for the title complexes are different from those of the corresponding *cis*-β_1 and β_2-salicylato(quadridentate amine)cobalt(III) complexes, *cis*-β_1, β_2-[Co(sal)L]Cl·nH$_2$O (L: trien, 2,3,2-tet, 3,2,3-tet, 3,3,3-tet), reported previously.

Previous papers[2,3] have been concerned with the preparation, properties, and NMR spectra of *cis*-β_1 and β_2-salicylato(quadridentate amine)cobalt(III) chloride hydrates, *cis*-β_1, β_2-[Co(sal)L]Cl·nH$_2$O (L: trien, 2,3,2-tet, 3,2,3-tet, 3,3,3-tet).

Many investigations[4—10] of the metal complexes with thiosalicylato (*o*-mercaptobenzoato) ligand have been concerned with the stability, formation constants, and potentiometric studies. However, the preparation of thiosalicylato metal complexes has not yet been described, except for Rh(thiosal)$_2$,[11] Ni(thiosal)$_2$,[12] [Pt(bpy)(thiosal)],[13] and (PPh$_4$)[Mn(thiosal)$_2$(HIm)][14] (HIm: imidazole). Little is known of the preparation and physical and general properties for octahedral thiosalicylato metal complexes, in contrast with those of octahedral salicylato cobalt complexes and the related complexes.[1—3,15—18] The present paper deals with the preparation and properties of *cis*-β_1 and β_2-thiosalicylato(quadridentate amine)cobalt(III) complexes, *cis*-β_1, β_2-[Co(thiosal)L]Cl·nH$_2$O (L: trien, 3,2,3-tet), and deals with the assignments of the configuration of cis-β_1 and β_2-isomers on their IR, NMR, and absorption spectra.

Experimental

Measurements. The electric conductivities in aqueous solutions were determined by the use of a conductometric meter, CM-30 (Shimadzu), at room temperature. The magnetic susceptibilities were measured by Faraday's method using a magnetic balance (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 ^{1}H 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. *cis*-α-Dichloro(triethylenetetramine)cobalt(III) Chloride (1) and *trans*-Dichloro(4,7-diazadecane-1,10-diamine)cobalt(III) Chloride Hydrate (2): These complexes were prepared by the methods of Sargeson[19] and Bosnich.[20]

***cis*-β_1-Thiosalicylato(triethylenetetramine)cobalt(III) Chloride Hydrate (3) and β_2-Thiosalicylato(triethylenetetramine)cobalt(III) Chloride Trihydrate (4):** Complex **1** (5.0 g, 16.05 mmol) was added to moistend fresh Ag$_2$O, which was made from silver nitrate (5.5 g, 32.10 mmol) and potassium hydroxide (1.80 g, 32.10 mmol). The mixture was stirred for several minutes at room temperature; to the mixture was added 20 cm^3 of water and kept for about 30 min at 60 °C. The precipitated silver chloride was filtered off. Then, thiosalicylic acid (2.5 g, 16.2 mmol) and 3 cm^3 of 28% aqueous ammonia were added to the solution. From the reaction mixture, complexes **3** and **4** were obtained according to the following methods 1—3.

Method 1: The reaction mixture was stirred at 50 °C for 6 h; it was then concentrated on a rotary evaporator and dried. Yield: 6.38 g for *cis*-β-[Co(thiosal)trien]Cl·nH$_2$O. *cis*-β-[Co(thiosal)trien]Cl·nH$_2$O of 0.8 g was dissolved in 2 cm^3 of water, and the solution was injected onto a column of ion-exchange resin (Dowex 50W-X2, ϕ2.5×30 cm). Upon elution with 0.1 mol dm^{-3} NaCl, the effluent of the first russet band of complex **4** and that of the second russet band of complex **3** was collected and concentrated, respectively. The separated NaCl was removed. The purification for complexes **3** and **4** was recrystallized from water-acetone. Yields: 2.61 g (39.5%) for **3**, 2.30 g (32.0%) for **4**.

Method 2: The reaction mixture was stirred at 40 °C for 3 h, and allowed to remain one night in an icebox; then the precipitated complex **3** was filtered and recrystallized. To the filtrate was added ethanol; the mixture was allowed to remain one night. The precipitated complex **4** was filtered and recrystallized from water–acetone. Yields: 1.0 g (15.2%) for **3**, 2.6 g (36.1%) for **4**.

Method 3: The reaction mixture was stirred at 60 °C for 6 h, and concentrated on a rotary evaporator. A little water was added to the reaction mixture, and the separated complex **3** filtered and recrystallized from water–acetone. To the filtrate was added ethanol. The separated complex **4** was filtered, and recrystallized from water–acetone. Yields: 3.2 g (48.5 %) for **3**, 0.9 g (13.6%) for **4**. Color: dark russet for **3** and violet russet for **4**. Found **3**: C, 38.30; H, 6.07; N, 13.43; Cl, 9.12%. Calcd for $CoC_{13}H_{24}N_4O_3SCl$ (MW 410.81) C, 38.01; H, 5.89; N, 13.64; Cl, 8.63%. Found **4**: C, 34.93; H, 6.43; N, 12.89; Cl, 8.53%. Calcd for $CoC_{13}H_{28}N_4O_5SCl$ (MW 446.84) C, 34.94; H, 6.32; N, 12.54; Cl, 7.93%. Mp: 241 °C for **3**, 233 °C for **4**. Λ=130 for **3** and 118 S cm^2 mol^{-1} for **4** in water. IR spectra: 994, 1034, 1054, 1078, 1094 cm^{-1}, and 3040, 3112, 3204, 3272 cm^{-1} for **3**, 1000, 1034, 1056, 1066, 1080 cm^{-1}, and 3070, 3116, 3200, 3280 cm^{-1} for **4**.

Complexes **3** and **4** did not isomerize to **4** and **3**, respectively, in water or aqueous ammonia (pH≒10) at 20 °C after for 24 h, though **3** and **4** did isomerize to **4** and **3**, respectively, in water at 40 °C after for 24 h.

***cis*-β_1 and β_2-Thiosalicylato(4,7-diazadecane-1,10-diamine)cobalt(III) Chloride Hydrate (cis-β_1 (5), β_2 (6)):** Complex 2 (5.8 g, 16.2 mmol) was added to moistend fresh Ag_2O, which was made from silver nitrate (5.5 g, 32.1 mmol) and potassium hydroxide (1.8 g, 32.1 mmol). The mixture was stirred for several minutes at room temperature before adding 20 cm^3 of water. The mixture was left for about 30 min at 60 °C. The precipitated silver chloride was filtered off. Then, thiosalicylic acid (2.5 g, 16.2 mmol) and 3 cm^3 of 28% aqueous ammonia were added to the solution. From the reaction mixtures, complexes **5** and **6** were obtained according to the methods described in 1—2.

Method 1: The reaction mixture was stirred at 40 °C for 6 h, and concentrated on a rotary evaporator. The concentrated solution was injected on a column chromatograph on alumina. Upon elution with ethanol, the first green band was collected and concentrated on a rotary evaporator. The solution was cooled in an icebox; separated complex **5** was filtered and recrystallized. The filtrate was concentrated and dried. The dried product (0.8 g) was dissolved in 2 cm^3 of water. This solution was injected onto a column of ion-exchange resin (Dowex 50W-X2, ϕ2.5× 30 cm). On elution with 0.1 mol dm^{-3} NaCl, the effluent of the first green band of complex **6** and that of the second green band of complex **5** was collected and concentrated, respectively. The separated NaCl was removed. Complex **5** was recrystallized from water–methanol (1 : 7) and complex **6** was recrystallized from ethanol. Yields: 3.3 g (46.5%) for **5**, 0.8 g (11.3%) for **6**.

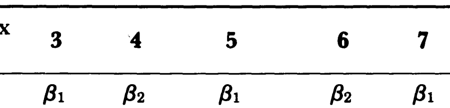
Method 2: The reaction mixture was stirred at 50 °C at 6 h and then concentrated on a rotary evaporator. The concentrated solution was injected onto a column chromatograph on alumina on elution with ethanol; the green band was collected and concentrated on a rotary evaporator. The solution was allowed to remain one night in an icebox. The precipitated complex **5** was filtered. From the filtrate of **5**, separation of **5** and **6** was achieved by a column of ion-exchange resin of the method 1. Yields: 3.45 g (48.5%) for **5**, 0.21 g (3.0%) for **6**. Color: greenish gray for **5** and **6**. Found **5**: C, 41.18; H, 6.67; N, 12.82; Cl, 8.11%. Found **6**: C, 41.15; H, 6.63; N, 13.01; Cl, 8.36%. Calcd for $CoC_{15}H_{28}N_4O_3SCl$ (MW 438.86) C, 41.05; H, 6.43; N, 12.77; Cl, 8.08%. Mp: 234 °C for **5** and **6**. Λ=105 for **5** and 110 S cm^2 mol^{-1} for **6** in water. IR spectra: 1018, 1036, 1052, 1067 cm^{-1}, and 3060, 3120, 3200, 3276 cm^{-1} for **5**, 1014, 1038, 1056, 1088 cm^{-1}, and 3084, 3160, 3192, 3260 cm^{-1} for **6**. Complexes **5** and **6** isomerize to **6** and **5**, respectively in water at 40 °C after for 24 h.

***cis*-β_1-Thiosalicylato(triethylenetetramine)cobalt(III) Nitrate Hydrate (7) and *cis*-β_2-Thiosalicylato(triethylenetetramine)cobalt(III) Nitrate Dihydrate (8):** Complexes **7** and **8** were prepared from the reaction mixture of silver nitrate (0.20 g, 1.20 mmol) and **3** (0.49 g, 1.19 mmol) or **4** (0.53 g, 1.19 mmol) in water, respectively. They were recrystallized from water–acetone and were unstable in 1.8 mol dm^{-3} and 3.6 mol dm^{-3} D_2SO_4 solution. Yields: 0.22 g (42.3%) for **7**, 0.25 g (46.3%) for **8**. Color: grayish russet for **7** and **8**. Found **7**: C, 35.87; H, 5.72; N, 16.27%. Calcd for $CoC_{13}H_{24}N_5O_6S$ (MW 437.37) C, 35.70; H, 5.53; N, 16.01%. Found **8**: C, 34.49; H, 6.02; N, 15.32%. Calcd for $CoC_{13}H_{26}N_5O_7S$ (MW 455.38) C, 34.29; H, 5.76; N, 15.38%. Mp: 230 °C for **7**, 227 °C for **8**. Λ=107 for **7** and 103 S cm^2 mol^{-1} for **8** in water. IR spectra: 999, 1035, 1068, 1088 cm^{-1}, and 3115, 3145, 3210, 3255 cm^{-1} for **7**, 990, 1035, 1065, 1077 cm^{-1}, and 3105, 3160, 3190, 3240 cm^{-1} for **8**. Absorption spectra: 294 nm (ε=12000),415 sh, 533 (250), and 580 (235) for **7**, 295 nm (ε=12500) and 570 (315) for **8** in water.

Results and Discussion

***cis*-β_1 and β_2-Thiosalicylato(quadridentate amine)cobalt(III) Chloride Hydrates:** Abbreviations of the thiosalicylato(quadridentate amine)cobalt(III) complexes studied in this paper are listed in Table 1. Octahedral thiosalicylato(quadridentate amine)cobalt(III) complexes exist in three isomeric forms of cis-α, cis-β_1, and cis-β_2, as shown in Fig. 1. A mixture of *cis*-β_1 and β_2-thiosalicylato(quadridentate amine)cobalt(III) chloride hydrates has been obtained from a reaction mixture of complex **1** or **2**, Ag_2O, thiosalicylic acid and 28% aqueous ammonia. Two geometrical isomers (cis-β_1 (**3** and **5**) and cis-β_2 (**4** and **6**)) of their complexes were separated by Dowex 50W-X2 column chromatography. The *cis*-β_1 and β_2-thiosalicylato(trien)cobalt(III) nitrate hydrate (**7** and **8**) have been prepared from the reaction mixture of silver nitrate and the

Table 1. The Abbreviations of the Thiosalicylato(quadridentate amine)cobalt(III) Complexes



Complex No.	**3**	**4**	**5**	**6**	**7**	**8**
Form	β_1	β_2	β_1	β_2	β_1	β_2
L	trien	trien	3,2,3-tet	3,2,3-tet	trien	trien
X	Cl	Cl	Cl	Cl	NO_3	NO_3
n	1	3	1	1	1	2

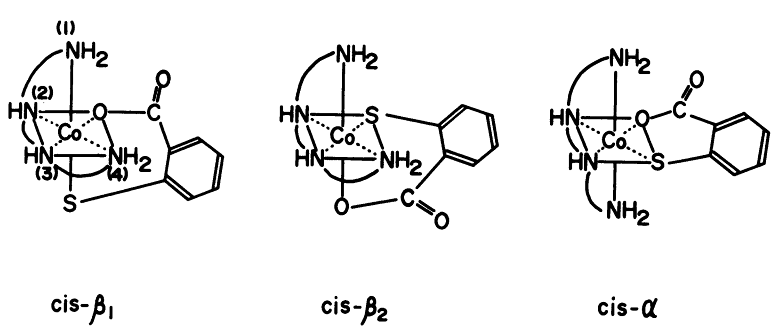


Fig. 1. The cis-α, β_1, and β_2 configurations of thiosalicylato(quadridentate amine)cobalt(III) complexes.

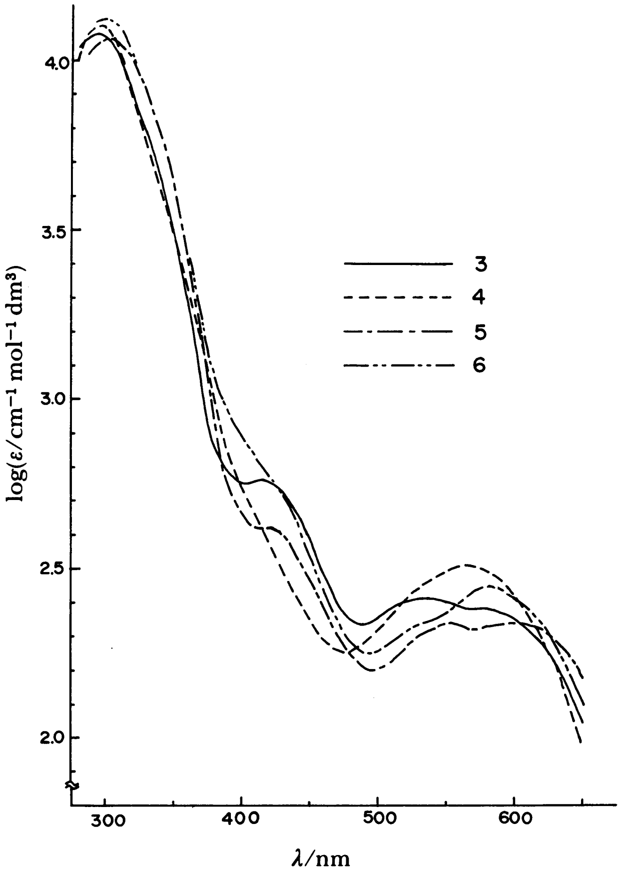


Fig. 2. The absorption spectra of complexes **3**—**6** in water.
3: *cis*-β_1-[Co(thiosal)trien]Cl·H_2O. **4**: *cis*-β_2-[Co(thiosal)trien]Cl·$3H_2O$. **5**: *cis*-β_1-[Co(thiosal)3,2,3-tet]Cl·H_2O. **6**: *cis*-β_2-[Co(thiosal)3,2,3-tet]Cl·H_2O.

corresponding chloride complexes (**3** and **4**). Complex **3** is soluble in water, and complexes **4**—**6** are very soluble in water. Complexes **3**—**6** are very soluble in methanol and DMSO, and soluble in ethanol but insoluble in the other common organic solvents, such as acetone and ether. The isomerization between **3** and **4** or **5** and **6** was reversible in water at 40 °C. Complexes **3** and **4** were diamagnetic, indicated by the magnetic susceptibility. The electric conductivities for **3**—**6** in aqueous solutions were 103—130 S cm^2 mol^{-1}.

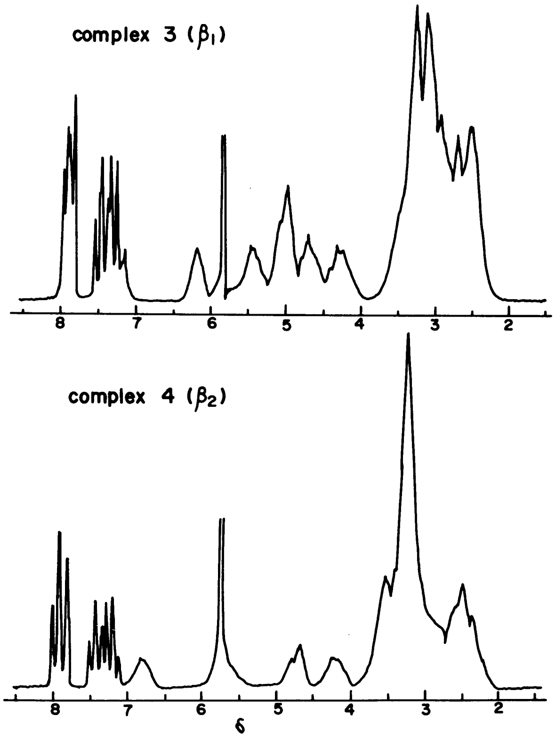


Fig. 3. The ^{1}H NMR spectra of complexes **3** and **4** in 1.8 mol dm^{-3} D_2SO_4.
3: *cis*-β_1-[Co(thiosal)trien]Cl·H_2O. **4**: *cis*-β_2-[Co(thiosal)trien]Cl·$3H_2O$.

The absorption spectra of **3**—**6** were measured in water, as shown in Fig. 2. The absorption bands at around 300 nm of **3**—**6** were assigned to the charge transfer band for the S-Co(III) bond.[21—23] The absorption bands at the 570—590 nm region for **4** and **6** are assigned to the first absorption band,[23] and those at 530—560 and 580—600 nm regions for **3** and **5** can be assigned to the split first absorption band.[24—26]

The ^{1}H NMR spectra of **3**—**6** were measured in 1.8 mol dm^{-3} D_2SO_4, as shown in Fig. 3. The signals at δ 2.1—3.8 and 3.6—6.8 of **3**—**6** were assigned to the methylene protons and amine protons of the coordinated quadridentate amine ligand respectively, and the lowest field signals at δ 7.0—8.1 were assigned to the coordinated thiosalicylato protons.[13] The signals of

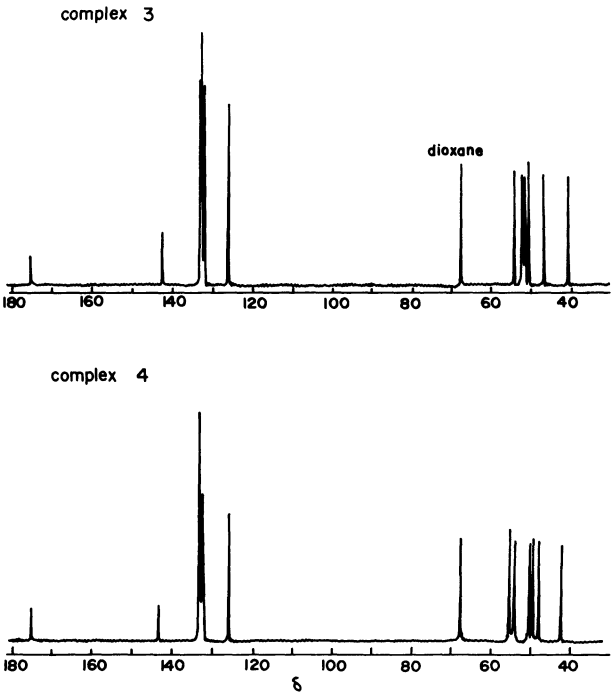


Fig. 4. The ^{13}C NMR spectra of complexes **3** and **4** in water.
3: *cis*-β_1-[Co(thiosal)trien]Cl·H_2O. **4**: *cis*-β_2-[Co(thiosal)trien]Cl·3H_2O.

the center, NH_2– side, and NH– side methylene protons and of the primary and secondary amine protons of **3**—**6** have been assigned by comparisons with those of *cis*-β_1- and β_2-salicylato(quadridentate amine)cobalt(III) chloride hydrate, *cis*-β_1, β_2-[Co(sal)L]Cl·$n$$H_2O$ (L: trien (β_1:**9**, β_2:**10**); 3,2,3-tet (β_2:**11**)),[2,3] and collected in Table 2. The signals of the primary and secondary amine protons of **3** and **4** disappeared in heavy water.

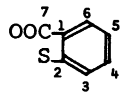
The ^{13}C NMR spectra of **3**—**6** were measured in D_2O, as shown in Fig. 4 and Table 2. There have been observed 6—8 signals for the quadridentate amine ligands and 5—7 signals for the thiosalicylato ligand. The chemical shifts of the coordinated thiosalicylato ligand in **3**—**6** and of thiosalicylic acid have been assigned by comparisons with those of the coordinated salicylato ligand in **9**—**11**[2,3] and salicylic acid,[17] respectively. On the other hand, the chemical shifts of the coordinated quadridentate amine ligands are difficult to assign to the individual carbon atoms; however, regions of the chemical shifts of the center, NH_2– side, and NH– side methylene carbons are around δ 21—28, 37—48, and 49—57, respectively, and their regions are close to those of **9**—**11**,[2,3] as shown in Table 2.

A distinction between **3** and **4** or **5** and **6** was found in the IR, NMR, and absorption spectra. The IR spectra of **3**—**6** showed four absorption bands in the NH stretching region (3000—3300 cm^{-1}) and four or five absorption bands in the NH_2 twisting region (990—1100 cm^{-1}), as shown in Experimental section. The ^{13}C NMR spectra of **3**—**6** showed 6—8 signals for the quadridentate amine ligands. They indicate that these complexes assume the cis-β-form.[2,27] In the ^{1}H NMR spectra, the methylene proton signals for the trien ligand in **4** can be divided into two groups of the NH_2– side methylene protons at δ 2.1—2.7 and NH– side methylene protons at δ 2.7—3.5 regions, as shown in Fig. 3. However, those of **3** could not be divided into two groups. One proton in the NH_2– side methylene protons for **4** overlapps to the NH– side methylene protons, since the intensity ratio of both methylene proton signals is 3:9. Also, the chemical shift (δ 3.45—4.0) of the proton signal of the N(1)H_2 group of **4** is at a higher field than that (δ 4.28) of **3**, i.e., the N(1)H_2 group of **4** is considered to be at a position trans[2] to the carboxyl oxygen of the coordinated thiosalicylato ligand, which is more electronegative than the thiolato sulfur. In addition, the spectrum of **4** showed five peaks with an intensity ratio of 2:1:1:1:1 for the amine protons, while that of **3** showed five peaks with an intensity ratio of 1:1:2:1:1, as shown in Fig. 2 and Table 2. These properties of **4** and **3** are similar to those of **10** and **9**,[2] respectively, as shown in Table 2. Thus, complexes **4** and **3** have been assigned to the cis-β_2 and β_1-isomers, respectively. On the other hand, complexes **5** and **6** could not be assigned from the ^{1}H NMR spectra, but they can be assigned from results of the absorption spectra. For instance, complexes **3**—**6** give the first absorption band at nearly the same position, but the first absorption band of **5** differs remarkably from that of **6**, and the absorption bands of **5** and **6** are very close to those of **3** and **4**, respectively, as shown in Fig. 2. Also, the elution order of **5** and **6** is similar to that of **3** and **4**, respectively. Then, complexes **5** and **6** are assigned to the cis-β_1 and β_2-isomers, respectively.

Buckingham and Sargeson have been concerned with the ^{1}H NMR, absorption spectra, and X-ray diffraction of the diastereoisomers of *cis*-β_1 and β_2-glycinato(trien)cobalt(III) complexes,[28,29] *cis*-β_1, β_2-[Co(gly)trien]$^{2+}$ ions, (β_1-*RR,SS*: **12a**, β_1-*RS,SR*: **12b**; β_2-*RR,SS*: **13a**, β_2-*RS,SR*: **13b**). The difference (Δδ:0.5) of the chemical shifts for the N(1)H_2 protons in the ^{1}H NMR spectra of β_1 (**12**) and β_2 (**13**) is bigger than that (Δδ:0) of **12a** and **12b** or of **13a** and **13b**. The first absorption bands of **12a** and **13a** are close to those of **12b** and **13b**, respectively. If the same relation holds in **3** and **4**, the difference (Δδ:0.7) of the chemical shift for the N(1)H_2 protons of **3** and **4** is close to that of cis-β_1 (**12**) and β_2 (**13**). The first absorption band of **3** differs remarkably from that of **4**, i.e., complexes **3** and **4** could not be assigned to the diastereoisomers, and have been assigned to the cis-β_1 and β_2-isomers, respectively. Next, the differences of the chemical shifts of the both N(2)H and N(3)H protons of **12a** and **12b** which are in positions trans of O atom and N atom

Table 2. ^{1}H, ^{13}C NMR, and Absorption Spectra of Complexes **3—6** and **9—11**

^{1}H Complex No. (isomer)	x,y,z	$NH_2(CH_2)_xNH(CH_2)_yNH(CH_2)_zNH_2$ δ Center methylene protons	NH$_2$- side methylene protons [Center+NH$_2$-+NH-]	NH- side methylene protons [NH-+N(1)H$_2$]	N(1)H$_2$ [N(1)H$_2$+N(4)H$_2$]	N(4)H$_2$	N(3)H N(2)H [N(3)H+N(2)H]	Thiosalicylato δ	solvent	Absorption bands in water λ/nm (ε/cm^{-1} mol^{-1} dm^3)			
3(β_1)	2,2,2		2.20—3.75(12H) 2.20—3.80(12H) 2.30—3.55(12H)		4.28(1H) 4.70(1H) 4.20(1H) 4.60(1H)	4.96(2H) 4.86(2H)	5.45(1H) 6.20(1H) 5.20(1H) 6.10(1H)	7.1—8.1(4H) a) 7.1—7.9(4H)	1 2 3	295 (12000)	417sh	533 (260)	580 (240)
4(β_2)	2,2,2		2.12—2.70(3H) 2.25—2.75(3H) 2.20—2.77(3H)	2.70—3.45(9H) [2.75—3.82(11H)] 2.77—3.60(9H)	3.45—4.00(2H)	4.20(1H) 4.70(1H) 4.12(1H) 4.58(1H)	a) 6.80(1H) 5.67(1H) 6.67(1H)	7.0—8.1(4H) a) 7.1—7.9(4H)	1 2 3	295 (12700)			568 (320)
5(β_1)	3,2,3		[1.50—2.60(10H)] [1.50—2.58(10H)]	[2.60—3.70(7H)] [2.58—3.65(7H)]		[3.4—4.5(3H)] [3.8—4.5(3H)]	[5.70(2H)] [5.58(2H)]	7.1—8.1(4H) a)	1 2	302 (11800)	415sh	555 (220)	603 (220)
6(β_2)	3,2,3		[1.30—2.61(10H)] [1.40—2.60(10H)]	[2.61—3.60(7H)] [2.60—3.55(7H)]		[3.90(2H)] 4.28(1H) [3.75(2H)] 4.26(1H)	[5.50(2H)] [5.28(2H)]	7.1—8.1(4H) a)	1 2	300 (13200)		535sh[b]	588 (280)
9(β_1)[c]	2,2,2		2.39—3.76(12H)		4.34(1H) 4.57(1H)	4.81(1H) 5.23(1H)	6.20(1H) 6.51(1H)	6.7—8.0(4H)	1		331 (2960)	530 (270)	
10(β_2)[c]	2,2,2		2.38—2.80(3H)	2.80—3.80(9H)	4.34(2H)	4.76(1H) 5.21(1H)	6.07(1H)	[6.5—8.0(5H)]	1		333 (3050)	520 (270)	
11(β_2)[d]	3,2,3	1.44—1.97(4H)	1.97—2.40(3H)	2.40—3.20(9H)	3.32(1H) 4.14(1H)	4.71(2H)	5.12(1H) 6.31(1H)	6.6—8.0(4H)	1		335 (2420)	533 (217)	



^{13}C	$NH_2(CH_2)_xNH(CH_2)_yNH(CH_2)_zNH_2$ δ Center methylene carbon		NH$_2$- side methylene carbon		NH- side methylene carbon				δ C-1	C-2	C-3	C-4	C-5	C-6	C-7
3 (β_1)			40.4	46.8	50.3	51.3	52.0	53.9	125.7	142.4	125.7	133.0	131.7	132.6	175.2
4 (β_2)			41.8	47.6	49.0	49.8	53.5	54.9	125.5	143.3	125.5	133.0	132.1	133.0	175.6
5 (β_1)	21.7	26.2	37.0	38.3	44.6	46.1	47.4	51.7	126.1	143.1	125.8	133.2	132.0	132.9	175.2
6 (β_2)[e]	24.2	27.2	38.7	39.1	48.9	49.8	53.0	56.4	125.6	143.0	125.6	133.2	131.8	133.2	174.7
9 (β_1)[c]			43.6	45.8	51.9	52.1	53.9	56.9	118.6	167.8	117.4	134.3	124.2	132.4	174.6
10 (β_2)[c]			42.0	47.5	48.3	49.7	52.1	52.7	118.1	168.2	117.1	134.5	124.3	132.3	174.1
11 (β_2)[d]	21.9	27.2	37.0	38.5	45.2	47.6	48.3	52.9	117.1	168.2	116.6	134.4	124.4	132.2	174.1
L′									128.4	140.6	126.3	134.3	132.7	133.8	170.7
L″[f]									113.8	162.7	118.0	136.6	120.2	131.5	173.6

Solvent and standard: ^{1}H NMR: 1) 1.8 mol dm^{-3} D_2SO_4, 2) 3.6 mol dm^{-3} D_2SO_4, 3) D_2O, internal DSS (δ=0); ^{13}C NMR: **3—6**, **9—11**: D_2O, internal dioxane (δ=67.4): L′: thiosalicylic acid, L″: salicylic acid: MeOH-d_4 (δ=49.8). a) This signal overlapped with each solvent. b) Very week shoulder. c) Ref. 2. d) Ref. 3. e) This spectrum has small spectrum of **5**, because of isomerism in the measurement. f) Ref. 17.

are 0.8 and 0 ppm, respectively, while those of **13a** and **13b** which are in positions trans of N atom and N atom are 0.15 and 0.25 ppm, respectively. In the case of **3** and **4**, the differences of the chemical shifts of both the NH protons of **3** and **4** which are in positions trans S atom and N atom are 0.8 and 1.0 ppm, respectively. They are very close to that of **12a**. Thus, complexes **3** and **4** are tentatively assigned to the *cis*-β_1-*RR*,*SS*- and *cis*-β_2-*RR*,*SS*-[Co(thiosal)trien]Cl·nH$_2$O, respectively.

In the complexes **3**—**6**, the melting point and solubility of **3** and **4** are almost similar to those of **5** and **6**. However, the color of the solid state, formation ratio, and first absorption band of **3** and **4** are different from those of **5** and **6**, i.e., the formation ratio of **3** and **4** is ca. 4:3 at 50 °C but that of **5** and **6** is ca. 16:1 at 50 °C. The ε of the first absorption band of **3** and **4** is larger than that of **5** and **6**, respectively and their first absorption band shifts from 530—580 nm to 550—600 nm. These results are similar to those of **9**—**11**, and the related complexes, *cis*-β_1, β_2-[Co(sal)L]Cl·nH$_2$O (L: 2,3,2-tet (β_1: **14**, β_2: **15**), 3,3,3-tet (β_2:**16**)), i.e., it is attributable to the center methylenes of the quadridentate ligands.[3]

cis-β_1 and β_2-Thiosalicylato(trien)cobalt(III) Complexes (3 and 4) and cis-β_1 and β_2-Salicylato(trien)-cobalt(III) Complexes (9 and 10): The color of the solid state, solubilities in alcohols, formation ratio, isomerization, absorption and ^{13}C NMR spectra, and reaction in 60% nitric acid for **3** and **4** are different from those for **9** and **10**.[2] The color of **3** and **4** is dark russet and violet russet, respectively, but that of **9** and **10** is russet. The formation ratios of **3** and **4** are ca. 3:7 at 40 °C, ca. 4:3 at 50 °C and ca. 4:1 at 60 °C, i.e., the yield for **3** increases with a rise in reaction temperature. The formation ratio of **9** and **10** is ca. 1:20 at 50 °C. The isomerization between **3** and **4** is reversible in water at 40 °C, but isomerization between **9** and **10** is irreversible in water, i.e., complex **10** does not isomerize to **9** at 40 °C after for 24 h. The first absorption band of **3** showed at 533 and 580 nm, but that of **9** showed at 530 nm. The chemical shift (δ ca. 143) of C-2 carbon of the coordinated thiosalicylato ligand in **3** and **4** differs remarkably from that (δ ca. 168) of **9** and **10**. It can be affected by the electronic effect of the S atom of the coordinated thiosalicylato ligand. The paramagnetic 5-nitrothiosalicylato(trien)-cobalt(III) complexes could not be prepared from a reaction mixture of **3** or **4** and 60% nitric acid, while the paramagnetic *cis*-β_1 and β_2-5-nitrosalicylato(trien)-cobalt(III) complexes, *cis*-β_1,β_2-[Co(5-NO$_2$sal)trien]Cl·NO$_3$·2H$_2$O, were obtained from the reaction mixture of **9** or **10** and 60% nitric acid, reported previously.[18] These properties can be attributed to differences of the electronic effect and atomic radius of S and O atoms, and of the stability between the Co–S and Co–O bonds of coordinated ligands.

Some properties for complexes **3**—**6** and **9**—**11** are listed in Table 2 and Experimental section.

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