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Cobalt(III) Complexes with $[N_{6-n}X_n]$-Type Ligands. VII.[1] Preparation and Properties of Isomers of the (Salicylamidato)cobalt(III) Complexes with Tris(2-aminoethyl)amine, Triethylenetetramine, and Ethylenediamine Ligands

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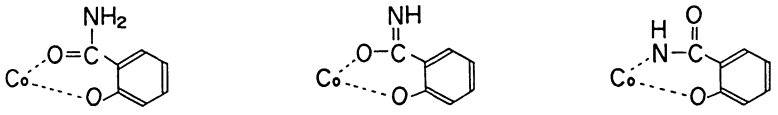
Title complexes of *t*- and *p*-[Co(**A**)(tren)]$Cl_2 \cdot H_2O$, *t*- and *p*-[Co(**C**)(tren)]$Cl \cdot H_2O$, *cis*-β_1 and β_2-[Co(**A**)(trien)]-$Cl_2 \cdot 2H_2O$, *cis*-β_1-[Co(**C**)(trien)]$Cl \cdot H_2O$, *cis*-β_1-[Co(**D**)(trien)]$Cl \cdot H_2O$, [Co(**A**)$(en)_2$]$Cl_2 \cdot H_2O$, [Co(**C**)$(en)_2$]$Cl \cdot H_2O$, and [Co(**D**)$(en)_2$]$Cl \cdot H_2O$ have been obtained from a reaction mixture of [$CoCl_2$L]$Cl \cdot H_2O$ [L: tren, trien, or $(en)_2$], Ag_2O, and salicylamide.



(A) (C) (D)

Separations of the **A**-, **C**-, and **D**-type complexes, and of the geometrical isomers of *t*- and *p*- or *cis*-β_1 and β_2 were attempted by using Dowex 50W-X2 column chromatography. Distinction of the **A**-, **C**-, and **D**-type complexes is described in the IR, ^1H, ^{13}C NMR, and absorption spectra; the solubility in DMSO; and the electric conductivities in aqueous solutions. The formation ratio of the **A**-, **C**-, and **D**-type complexes has been dependent upon the pH of the reaction mixture. The chemical shifts (δ=113—115) of the C-1 carbon signals for the **A**-type complexes are at a higher field than those (δ=117—122) of the **C**- and **D**-type complexes. The ε values (3400—3700) of the charge transfer band at ca. 340 nm in the absorption spectra for the **A**-type complexes are greater than those (2500—3000) of the **C**- and **D**-type complexes. The **C**-type and **D**-type complexes are a linkage isomer. A characteristic property of the linkage isomer has been observed in the absorption and ^{13}C NMR spectra as well as the solubility in DMSO.

We previously described the preparation, properties, and geometrical isomers of mixed-ligand (8-quinolinolato)-,[2-4] (salicylato)-,[5-7] (thiosalicylato)-,[8] or (salicylaldehydato)cobalt(III)[9,10] complexes with ethylenediamine (en), tris(2-aminoethyl)amine (tren), triethylenetetramine (trien), 3,7-diazanonane-1,9-diamine (2,3,2-tet), 4,7-diazadecane-1,10-diamine (3,2,3-tet), and 4,8-diazaundecane-1,11-diamine (3,3,3-tet) ligands. However, the preparation and properties of the mixed-ligand amine(salicylamidato)cobalt(III) complexes have not been of concern.

Salicylamide (*o*-hydroxybenzamide) is a very useful ligand in the field of coordination chemistry, since the $-CONH_2$ group of salicylamide can coordinate to a metal atom through the carbonyl oxygen (**A**-type) or the amide nitrogen (**B**-type), as is shown in Fig. 1. So far, bis- and tris(salicylamidato)metal complexes[11-13] of the **A**-type, $[M(A)_m]^{n+}$ [M: Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), or Hg(II); *m*: 2 or 3], have been reported concerning preparation, magnetic moments, IR spectra, and X-ray diffraction. However, the corresponding **B**-type complexes could not be prepared.

We recently succeeded in preparing the tetraamine(salicylamidato)cobalt(III) complex,[1] [Co(**D**)-$(NH_3)_4$]$Cl \cdot H_2O$, of the **D**-type, which is a bond between a cobalt atom and an imide nitrogen from a reaction mixture of $CoCl_2 \cdot 6H_2O$, aqueous ammonia, H_2O_2, and salicylamide. However, the **A**-, **B**-, and **C**-type complexes could not be obtained. Now, however, complexes of the **A**-, **C**-, and **D**-types have been prepared in this study. Thus, the present paper deals with the preparation and properties of the mixed-ligand amine-(salicylamidato)cobalt(III) complexes of [Co(**A**)L]$Cl_2 \cdot$

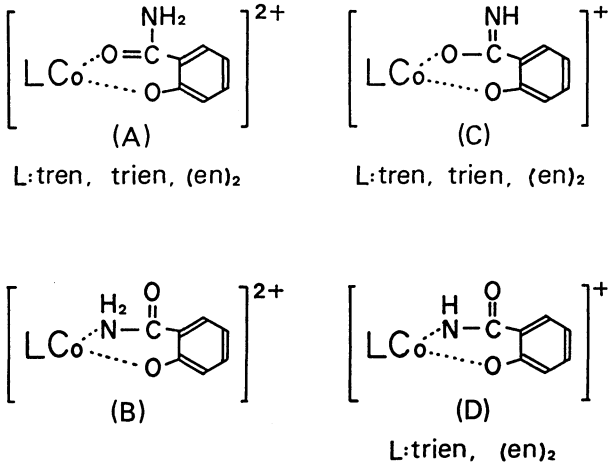


Fig. 1. Configurations of the **A**—**D**-type complexes of amine(salicylamidato)cobalt(III) complexes.

nH$_2$O [L: tren, trien, or (en)$_2$], [Co(**C**)L]Cl·H$_2$O [L: tren, trien, or (en)$_2$], and [Co(**D**)L]Cl·H$_2$O [L: trien or (en)$_2$].

Experimental

Measurements. The electric conductivities were determined by the use of a CM-40S conductivity meter (TOA) in aqueous solutions at room temperature. The IR spectra were recorded in KBr disks with a 270-30 spectrophotometer (Hitachi). The visible absorption spectra were recorded in water with a Shimadzu UV-210 recording spectrophotometer. The ^{1}H and ^{13}C NMR spectra were recorded with a JNM-FX90Q FT NMR spectrometer (JEOL). The melting points were measured on an MP-500D apparatus (Yanako).

Preparation of Complexes. *t*-(Salicylamidato-*O,O*)[tris(2-aminoethyl)amine]cobalt(III) Dichloride Hydrate (1), *p*-(Salicylamidato-*O,O*)[tris(2-aminoethyl)amine]cobalt(III) Dichloride Hydrate (2), *t*-(Salicylamidato-*O,O*)[tris(2-aminoethyl)amine]cobalt(III) Chloride Hydrate (3), and *p*-(Salicylamidato-*O,O*)[tris(2-aminoethyl)amine]cobalt(III) Chloride Hydrate (4): [CoCl$_2$tren]Cl·H$_2$O (10.0 g, 30.3 mmol) was added to moistend fresh Ag$_2$O, which was made from silver nitrate (10.3 g, 60.6 mmol) and potassium hydroxide (3.4 g, 60.6 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. A methanol solution (60 cm^3) of salicylamide (4.15 g, 30.3 mmol) was added, drop by drop, to the reddish-violet filtrate (pH 8.6). The solution was stirred for 12 h at 58 °C and was then concentrated on a rotary evaporator, and salicylamide (ca. 0.6 g) precipitated was filtered. The separation of complexes **1**—**4** was achieved by using a column (ϕ 2.5 cm×40 cm) of ion-exchange resin (Dowex 50W-X2, 100—200 mesh). Upon elution with 0.3 mol dm^{-3} NaCl, the effluents of the first reddish-brown band (complex **3**) and second red band (complex **4**) were collected and concentrated, respectively. Then, the third red band (complex **1**) and fourth red band (complex **2**) were eluted with 0.8 mol dm^{-3} NaCl and concentrated, respectively. Complexes **1**—**4** were recrystallized from water-ethanol-ether. Yields: 2.6 g (19.9%) for **1**, 3.8 g (29.2%) for **2**, 0.53 g (4.4%) for **3**, 0.38 g (3.2%) for **4**. Found **1**: C, 36.35; H, 6.11; N, 16.44; Cl, 16.59%. **2**: C, 36.55; H, 6.27; N, 16.31; Cl, 16.70%. Calcd for $CoC_{13}H_{26}N_5O_3Cl_2$ (MW 430.22): C, 36.29; H, 6.09; N, 16.28; Cl, 16.48%. Found **3**: C, 39.59; H, 6.55; N, 17.51; Cl, 9.23%. **4**: C, 39.74; H, 6.58; N, 17.56; Cl, 9.29%. Calcd for $CoC_{13}H_{25}N_5O_3Cl$ (MW 393.76): C, 39.65; H, 6.40; N, 17.79; Cl, 9.00%. ^{1}H NMR **1**: δ=2.60—3.07 (4H, NH$_2$- side CH$_2$), 3.07—3.90 (8H, NH$_2$- and N- side CH$_2$); 4.75 (6H, NH$_2$); 6.7—7.8 (4H, salicylamidato) in 1.8 mol dm^{-3} D$_2$SO$_4$. δ=2.5—3.5 (12H, CH$_2$); 5.12 (2H), 5.85 (4H), each NH$_2$; 6.3—7.9 (4H, salicylamidato); 8.85, 8.92 (each 1H, -CONH$_2$) in DMSO-d_6. **2**: δ=2.50—2.80 (2H, NH$_2$- side CH$_2$), 2.80—3.45 (6H, NH$_2$- and N- side CH$_2$), 3.45—3.90 (4H, N- side CH$_2$); 4.69 (4H), 5.04 (2H), each NH$_2$; 6.7—7.7 (4H, salicylamidato) in 1.8 mol dm^{-3} D$_2$SO$_4$. δ=2.5—3.5 (12H, CH$_2$); 4.85 (2H), 6.14 (4H), each NH$_2$; 6.4—7.9 (4H, salicylamidato); 8.70, 8.84 (each 1H, -CONH$_2$) in DMSO-d_6. **3**: δ=2.70—3.05 (4H, NH$_2$- side CH$_2$), 3.05—3.85 (8H, NH$_2$- and N- side CH$_2$); 5.00 (6H, NH$_2$); 6.6—7.9 (4H, salicylamidato) in 1.8 mol dm^{-3} D$_2$SO$_4$. δ=2.4—3.5 (12H, CH$_2$); 4.61 (2H), 5.25 (4H), each NH$_2$; 6.2—7.9 (4H, salicylamidato) in DMSO-d_6. **4**: δ=2.44—2.77 (2H, NH$_2$- side CH$_2$), 2.77—3.39 (6H, NH$_2$- and N- side CH$_2$), 3.39—4.00 (4H, N- side CH$_2$); 4.85 (4H), 5.10 (2H), each NH$_2$; 6.5—7.9 (4H, salicylamidato) in 1.8 mol dm^{-3} D$_2$SO$_4$. δ=2.4—3.6 (12H, CH$_2$); 4.50 (2H), 5.51 (4H), each NH$_2$; 6.3—7.9 (4H, salicylamidato) in DMSO-d_6. ^{13}C NMR (D$_2$O) **1**: δ=44.3, 45.4, 45.4 (each NH$_2$- side CH$_2$), 60.8, 61.8, 61.8 (each N- side CH$_2$); δ=114.3 (C-1), 167.2 (C-2), 118.1 (C-3), 136.4 (C-4), 124.8 (C-5), 130.0 (C-6), 173.1 (C-7). **2**: δ=43.6, 45.2, 45.2 (each NH$_2$- side CH$_2$), 61.7, 62.0, 62.0 (each N- side CH$_2$); δ=113.1 (C-1), 166.7 (C-2), 117.6 (C-3), 136.1 (C-4), 125.7 (C-5), 129.6 (C-6), 173.4 (C-7). **3**: δ=44.0, 45.4, 45.4 (each NH$_2$- side CH$_2$), 60.7, 61.4, 61.4 (each N- side CH$_2$); δ=118.7 (C-1), 167.9 (C-2), 117.3 (C-3), 134.6 (C-4), 123.6 (C-5), 132.6 (C-6), 174.0 (C-7). **4**: δ=43.5, 45.3, 45.3 (each NH$_2$- side CH$_2$), 61.3, 61.6, 61.6 (each N- side CH$_2$), δ=117.4 (C-1), 167.7 (C-2), 117.0 (C-3), 134.6 (C-4), 124.8 (C-5), 132.4 (C-6), 174.6 (C-7). Mp: 242 for **1**, 207 for **2**, 238 for **3**, 250 °C for **4**.

***cis*-β_1-(Salicylamidato-*O,O*)(triethylenetetramine)cobalt(III) Dichloride Dihydrate (5), *cis*-β_2-(Salicylamidato-*O,O*)-(triethylenetetramine)cobalt(III) Dichloride Dihydrate (6), *cis*-β_1-(Salicylamidato-*O,O*)(triethylenetetramine)cobalt(III) Chloride Hydrate (7), *cis*-β_2-(Salicylamidato-*O,O*)(triethylenetetramine)cobalt(III) Chloride Hydrate (8), and *cis*-β_1-(Salicylamidato-*N,O*)(triethylenetetramine)cobalt(III) Chloride Hydrate (9):** A mixture of complexes **5**—**9** was prepared from a reaction mixture (pH 8.6) of [CoCl$_2$(trien)]Cl (10.0 g, 32.1 mmol), fresh Ag$_2$O (7.44 g, 32.1 mmol), and salicylamide (4.4 g, 32.1 mmol) according to the procedure for complexes **1**—**4**. The separation of complexes **5**—**9** was achieved by a column (ϕ 2.5 cm×30 cm) of ion-exchange resin (Dowex 50W-X2, 100-200 mesh). Upon elution with 0.2 mol dm^{-3} NaCl, the effluents of the first reddish-violet band (mixture of complexes **7** and **8**) and second red band (complex **9**) were collected and concentrated, respectively. Then, upon elution with 0.6 mol dm^{-3} NaCl, the effluents of the third red band (complex **5**) and fourth red band (complex **6**) were collected and concentrated, respectively. The separation of complexes **7** and **8** from the first reddish-violet band was achieved by a column (ϕ 2.5 cm×40 cm) of ion-exchange resin (Dowex 50W-X2, 200—400 mesh). Upon elution with 0.1 mol dm^{-3} NaCl, the effluents of the lower (**7**) and upper (**8**) layers of the reddish-violet band were collected and concentrated, respectively. Complex **7** was isolated; pure complex **8** was not obtained, however, because of isomerization to **7**. Complexes **5**—**7** and **9** were recrystallized from water-ethanol-ether or water-ethanol-acetone. Yields: 2.1 g (14.6%) for **5**, 2.3 g (16.0%) for **6**, 1.1 g (8.7%) for **7**, 0.35 g (2.8%) for **9**, recovered salicylamide: 0.85 g. Found **5**: C, 34.60; H, 6.52; N, 15.80; Cl, 15.80%. **6**: C, 34.57; H, 6.55; N, 15.66; Cl, 16.06%. Calcd for $CoC_{13}H_{28}N_5O_4Cl_2$ (MW 448.23): C, 34.83; H, 6.30; N, 15.63; Cl, 15.82%. Found **7**: C, 39.92; H, 6.57; N, 17.56; Cl, 9.14%. Calcd for $CoC_{13}H_{25}N_5O_3Cl$ (MW 393.76): C, 39.65; H, 6.40; N, 17.79; Cl, 9.00%. Found **9**: C, 39.84; H, 6.42; N, 17.88; Cl, 9.30%. Calcd for $CoC_{13}H_{25}N_5O_3Cl$ (MW 393.76): C, 39.65; H, 6.40; N, 17.79; Cl, 9.00%. IR **5**: 3108, 3130, 3184, 3200 cm^{-1} (NH stretch.); 1000, 1030, 1056, 1080 cm^{-1} (NH$_2$ twist.). **6**: 3100, 3200, 3248, 3288 cm^{-1} (NH stretch.); 1002, 1036, 1052, 1078 cm^{-1} (NH$_2$ twist.). **7**: 3090, 3150, 3200, 3240 cm^{-1} (NH stretch.); 1002, 1043, 1052, 1074 cm^{-1} (NH$_2$ twist.). **9**: 3040, 3130, 3180, 3226 cm^{-1} (NH stretch.); 999, 1038, 1077, 1100 cm^{-1} (NH$_2$ twist.). ^{1}H NMR **5**: δ=2.35—3.60 (12H, NH$_2$- and NH- side CH$_2$); 4.24 (2H,

N(1)H_2), 4.5—5.2 (2H, N(4)H_2); 6.22 (2H, N(2)H and N(3)H); 6.7—7.8 (4H, salicylamidato) in 1.8 mol dm^{-3} D_2SO_4. δ=2.15—3.28 (12H, CH_2); 3.84 (1H), 5.11 (2H), 5.51 (1H), each NH_2; 6.95, 8.20 (each 1H, NH); 6.4—7.9 (4H, salicylamidato); 8.89, 8.96 (each 1H, -$CONH_2$) in DMSO-d_6. **6**: δ=2.38—2.78 (3H, NH_2- side CH_2), 2.78—3.65 (9H, NH_2- and NH- side CH_2); 4.30 (3H, N(1)H_2 and N(4)H_2), 5.01 (1H, N(4)H_2), 5.95 (N(2)H), 6.30 (N(3)H); 6.6—7.7 (4H, salicylamidato) in 1.8 mol dm^{-3} D_2SO_4. δ=2.10—2.60 (3H), 2.60—3.27 (9H), each CH_2; 3.95, 4.69, 5.37, 5.85 (each 1H, NH_2), 7.00, 8.23 (each 1H, NH); 6.4—7.9 (4H, salicylamidato); 8.68, 8.95 (each 1H, -$CONH_2$) in DMSO-d_6. **7**: δ=2.30—3.60 (12H, NH_2- and NH- side CH_2); 4.70 (4H, N(1)H_2 and N(4)H_2), 5.90 (2H, N(2)H and N(3)H); 6.6—7.9 (4H, salicylamidato) in 1.8 mol dm^{-3} D_2SO_4. δ=2.10—3.25 (12H, CH_2); 3.7—4.3 (2H), 4.5—5.2 (2H), each NH_2; 5.52, 6.10 (each 1H, NH); 6.2—7.9 (4H, salicylamidato) in DMSO-d_6. **9**: δ=2.32—3.64 (12H, NH_2- and NH- side CH_2); 3.64—4.49 (4H, N(1)H_2, N(4)H_2, and -CONH), 4.65 (1H, N(4)H_2), 5.76 (N(2)H), 6.18 (N(3)H); 6.6—7.9 (4H, salicylamidato) in 1.8 mol dm^{-3} D_2SO_4. δ= 1.90—3.25 (13H, CH_2 and NH_2), 4.22 (1H), 4.53 (2H), each NH_2; 4.89 (1H, -CONH); 5.43, 7.61 (each 1H, NH); 6.2—7.9 (4H, salicylamidato) in DMSO-d_6. ^{13}C NMR (D_2O) **5**: δ= 42.7, 47.8 (each NH_2- side CH_2), 48.4, 49.9, 51.9, 53.0 (each NH- side CH_2); δ=115.0 (C-1), 167.3 (C-2), 117.9 (C-3), 136.3 (C-4), 125.0 (C-5), 129.8 (C-6), 173.3 (C-7). **6**: δ=42.3, 47.5 (each NH_2- side CH_2); δ=48.6, 50.0, 52.3, 52.7 (each NH- side CH_2); δ=114.2 (C-1), 167.4 (C-2), 117.6 (C-3), 136.1 (C-4), 125.4 (C-5), 129.6 (C-6), 173.0 (C-7). **7**: δ=41.4, 47.0 (each NH_2- side CH_2), 48.9, 50.0, 52.4, 53.0 (each NH- side CH_2); δ=117.3 (C-1), 165.9 (C-2), 117.6 (C-3), 133.5 (C-4), 123.6 (C-5), 130.7 (C-6), 172.9 (C-7). **9**: δ=41.4, 48.0 (each NH_2- side CH_2), 48.3, 49.3, 52.8, 53.6 (each NH- side CH_2); δ=121.5 (C-1), 166.7 (C-2), 117.0 (C-3), 133.3 (C-4), 123.7 (C-5), 130.5 (C-6), 172.5 (C-7). Mp: 217 for **5**, 225 for **6**, 230 for **7**, 244 °C for **9**.

Bis(ethylenediamine)(salicylamidato-*O,O*)cobalt(III) Dichloride Hydrate (10), Bis(ethylenediamine)(salicylamidato-*O,O*)cobalt(III) Chloride Hydrate (11), and Bis(ethylenediamine)(salicylamidato-*N,O*)cobalt(III) Chloride Hydrate (12): A mixture of complexes **10**—**12** was prepared from the reaction mixture (pH 8.6) of $[CoCl_2(en)_2]Cl$ (10.0 g, 35.0 mmol), fresh Ag_2O (8.11 g, 35.0 mmol), and salicylamide (4.8 g, 35.0 mmol) according to the procedure for complexes **1**—**4**. The separation of complexes **10**—**12** was achieved by a column (ϕ 2.5 cm×20 cm) of ion-exchange resin (Dowex 50W-X2, 100—200 mesh). Upon elution with 0.2 mol dm^{-3} NaCl, the effluent of the first red band (mixture of **11** and **12**) was collected and concentrated. Then, the second red band (**10**) was eluted with 0.8 mol dm^{-3} NaCl. The effluent of **10** was collected and concentrated. The separation of **11** and **12** was achieved by a column (ϕ 2.5 cm×40 cm) of ion-exchange resin (Dowex 50W-X2, 200—400 mesh). Upon elution with 0.1 mol dm^{-3} NaCl, the effluents of the lower (**11**) and upper (**12**) layers of the red band were collected and concentrated, respectively. Complexes **10**—**12** were recrystallized from water-ethanol-ether. Yields: 5.31 g (37.5%) for **10**, 0.6 g (4.7%) for **11**, 0.3 g (2.3%) for **12**. Found **10**: C, 32.72; H, 5.88; N, 17.19; Cl, 17.78%. Calcd for $CoC_{11}H_{24}N_5O_3Cl_2$ (MW 404.18): C, 32.69; H, 5.99; N, 17.33; Cl, 17.54%. Found **11**: C, 36.19; H, 6.52; N, 19.18; Cl, 9.78%. **12**: C, 36.04; H, 6.22; N, 18.98; Cl, 9.87%. Calcd for $CoC_{11}H_{23}N_5O_3Cl$ (MW 367.72): C, 35.93; N, 6.30; N, 19.05; Cl, 9.64%. ^{1}H NMR **10**: δ=2.76, 2.84 (each 4H, CH_2); 4.17 (2H), 4.30—4.75 (3H), 4.95 (1H), 5.16 (2H), each NH_2; 6.7—7.7 (4H, salicylamidato) in 1.8 mol dm^{-3} D_2SO_4. δ=2.3—2.8 (8H, CH_2); 4.21 (1H), 4.42 (1H), 5.00 (1H), 5.25 (1H), 5.45—6.20 (4H), each NH_2; 6.4—7.9 (4H, salicylamidato); 8.58, 8.80 (each 1H, -$CONH_2$) in DMSO-d_6. **11**: δ=2.85 (8H, CH_2); 4.26 (2H), 4.50 (2H), 4.96 (1H), 5.27 (3H), each NH_2; 6.4—7.9 (4H, salicylamidato) in 1.8 mol dm^{-3} D_2SO_4. δ=2.3—2.8 (8H, CH_2); 4.06 (2H), 4.63 (2H), 5.44 (4H), each NH_2; 6.2—7.9 (4H, salicylamidato) in DMSO-d_6. **12**: δ=2.75 (8H, CH_2); 3.93 (1H, -CONH); 4.28 (3H), 4.64 (5H), each NH_2; 6.6—7.9 (4H, salicylamidato) in 1.8 mol dm^{-3} D_2SO_4. δ=2.3—2.8 (8H, CH_2); 3.5—5.0 (7H, NH_2 and -CONH), 5.30 (2H, NH_2); 6.2—7.9 (4H, salicylamidato) in DMSO-d_6. ^{13}C NMR (D_2O) **10**: δ=43.7, 44.1, 45.6, 45.9 (each CH_2); δ=113.9 (C-1), 167.0 (C-2), 117.7 (C-3), 136.1 (C-4), 125.1 (C-5), 129.8 (C-6), 173.1 (C-7). **11**: δ=43.9, 43.9, 45.6, 45.7 (each CH_2); δ=118.1 (C-1), 167.7 (C-2), 117.2 (C-3), 134.5 (C-4), 124.0 (C-5), 132.6 (C-6), 174.2 (C-7). **12**: δ=44.8, 45.1 , 45.2, 45.4 (each CH_2); δ=120.7 (C-1), 166.4 (C-2), 117.0 (C-3), 133.2 (C-4), 123.6 (C-5), 130.6 (C-6), 172.5 (C-7). Mp: 218 for **10**, 245 for **11**, 256 °C for **12**.

Preparation of Complex 3 from 1 and of 4 from 2: Complex **1** (0.3 g, 6.97 mmol) was added to ammonia solution (6 cm^3, pH 10), and the mixture was stirred for 13 h at 62 °C. The solution was concentrated on a rotary evaporator. The purification of **3** was achieved by column chromatography on alumina. Complex **4** was also obtained from the mixture of **2** and ammonia solution. Yields: 0.22 g (80.1%) for **3**, 0.20 g (72.8%) for **4**.

Preparation of Complex 7 from 5 or 6: Complex **5** (1.0 g, 2.23 mmol) was added to an ammonia solution (15 cm^3, pH 10); the mixture was then stirred for 3 h at 62 °C, and concentrated on a rotary evaporator. The precipitated complex **7** was filtered. Yield: 0.64 g (72.9%).

Complex **6** (1.0 g, 2.23 mmol) was added to an ammonia solution (15 cm^3, pH 10); the mixture was then stirred for 12 h at 62 °C, concentrated, and the precipitated complex filtered. This complex was a mixture of complexes **7** and **8**. Complex **8** in the mixture became **7** after 5 h at 62 °C in solution, since **8** isomerizes to **7**. Yield: 0.56 g (63.7%).

Preparation of Complex 11 from 10: Complex **10** (1.0 g, 2.47 mmol) was added to an ammonia solution (15 cm^3, pH 10); the mixture was stirred for 13 h at 62 °C, and then concentrated on a rotary evaporator. The purification of **11** was achieved by column chromatography on alumina. Yield: 0.56 g (61.6%).

Solubility. All complexes were very soluble in water and soluble in methanol. For dimethyl sulfoxide (DMSO), complexes **1**, **2**, **5**, **6**, **9**, **10**, and **12** were soluble, but complexes **3**, **4**, **7**, and **11** were very slightly soluble. All of the complexes were not soluble in common organic solvents, such as acetone and ether.

Results and Discussion

The abbreviations of the octahedral amine(salicylamidato)cobalt(III) complexes in this research are listed in Table 1.

Complexes. Complexes **1**—**12** have been obtained from a reaction mixture of $[CoCl_2(L)]Cl \cdot nH_2O$ (L: tren, trien, $(en)_2$), Ag_2O, and salicylamide. Complexes **1**—**12** were separated by Dowex 50W-X2 column chromatography. The formation ratios of **1**, **2**, **3**, and **4** are ca.

Table 1. Abbreviations and Some Physical Properties of Complexes **1**—**7**, **9**—**12**, and **17**

No.	Complex	Electric conductivity of aqueous solution	IR (C=O)	^{13}C NMR[a] C-1	Absorption bands in water		
					λ/nm (ε/cm^{-1} mol^{-1} dm^3)		
		S cm^2 mol^{-1}	cm^{-1}	δ			
1	*t*-[Co(**A**)tren]Cl$_2$·H$_2$O	240	1644	114.3	340 (3720)	530 (275)	
2	*p*-[Co(**A**)tren]Cl$_2$·H$_2$O	250	1640	113.1	343 (3450)	510 (220)	
3	*t*-[Co(**C**)tren]Cl·H$_2$O	108	—	118.7	330 (2820)	535 (215)	
4	*p*-[Co(**C**)tren]Cl·H$_2$O	110	—	117.4	332 (3000)	515 (220)	
5	*cis*-β_1-[Co(**A**)trien]Cl$_2$·2H$_2$O	250	1644	115.0	340 (3410)	520 (315)	
6	*cis*-β_2-[Co(**A**)trien]Cl$_2$·2H$_2$O	245	1630	114.2	345 (3580)	512 (285)	
7	*cis*-β_1-[Co(**C**)trien]Cl·H$_2$O	115	—	117.3	320 (2500)	535 (260)	
9	*cis*-β_1-[Co(**D**)trien]Cl·H$_2$O	145	—	121.5	326 (2560)	510 (255)	535 (245)
10	[Co(**A**)(en)$_2$]Cl$_2$·H$_2$O	240	1644	113.9	342 (3600)	512 (235)	
11	[Co(**C**)(en)$_2$]Cl·H$_2$O	135	—	118.1	328 (2830)	517 (210)	
12	[Co(**D**)(en)$_2$]Cl·H$_2$O	140	—	120.7	326 (2790)	513 (210)	535 (200)
17[b]	[Co(**D**)(NH$_3$)$_4$]Cl·H$_2$O	113	—	120.0	323 (2790)	512 (185)	545 (180)

a) Solvent D$_2$O, standard dioxane (δ=67.4). b) Ref. 1.

6 : 9 : 1 : 1, respectively. The formation ratios of **5**, **6**, **7**, and **9** are ca. 5 : 6 : 3 : 1, respectively, and those of **10**, **11**, and **12** are ca. 16 : 2 : 1, respectively. The colors of **1** and **5** are russet. The colors of **2**, **4**, **7**, **10**, and **11** are red, and those of **3**, **6**, **9**, and **12** are brownish-violet, reddish-pink, reddish-violet, and reddish-brown, respectively.

The absorption spectra of all complexes were measured in water (Table 1). The absorption bands at ca. 340 nm of the complexes were assigned to the charge transfer band, while the bands at ca. 520 nm were assigned to the first absorption band[1] (Table 1). The ^{1}H NMR spectra of all complexes were measured in 1.8 mol dm^{-3} D_2SO_4 and in DMSO-d_6. The signals at δ=6.2—7.9 of the complexes were assigned to the ring protons of the coordinated salicylamidato ligand. The signals at δ=2.4—4.0 and 4.3—5.5 for **1**—**4** in 1.8 mol dm^{-3} D_2SO_4 were assigned to the methylene and amine protons of the coordinated tren ligand, respectively, by the comparisons with those of *t*- and *p*-salicylaldehydato(tren)cobalt(III) dichloride hydrate,[10] *t*-, *p*-[Co(salad)tren]Cl$_2$·H$_2$O (*t*: **13**, *p*: **14**). The methylene and amine protons of the coordinated trien ligand for **5**—**7** and **9** were assigned on the basis of those of *cis*-β_1 and β_2-salicylaldehydato(trien)cobalt(III) dichloride dihydrate,[9,10] *cis*-β_1, β_2-[Co(salad)trien]Cl$_2$·2H$_2$O (β_1: **15**, β_2: **16**). The signals at δ=2.7—2.9 and 4.1—5.3 for **10**—**12** have been assigned to methylene and amine protons of the coordinated ethylenediamine ligand, respectively. The ^{13}C NMR spectra of all complexes were measured in D$_2$O. Seven signals at δ=113—175 of the complexes were assigned to the carbons of the coordinated salicylamidato ligand by comparisons with those of tetraammine(salicylamidato)cobalt(III) chloride hydrate,[1] [Co(**D**)(NH$_3$)$_4$]Cl·H$_2$O (**17**). The signals at δ=43—45 and 60—62 for **1**—**4** were assigned to the NH$_2$- and N- side methylene carbons[7,10] of the coordinated tren ligand, respectively. The signals at δ=41—48 and 48—54 of **5**—**7** and **9** were assigned to the NH$_2$- and NH- side methylene carbons[6,10] of the coordinated trien ligand, respectively. The signals at δ=43—46 of **10**—**12** were assigned to the methylene carbons of the coordinated ethylenediamine ligand. The data are collected in the Experimental section.

The electric conductivities of **1** and **2** are ca. 240 S cm^2 mol^{-1} in aqueous solutions. The IR spectra of **1** and **2** show the C=O stretching vibration at 1640 cm^{-1}, which is lower than that (1680 cm^{-1}) of free salicylamide[13] in the solid state. This suggests that the carbonyl oxygen of the coordinated salicylamidato ligand of **1** and **2** is bonded to a cobalt atom.[11,13] The ^{1}H NMR spectra in DMSO-d_6 of **1** and **2** showed two singlet signals at δ=8.85 (1H) and 8.92 (1H) for **1** and δ=8.70 (1H) and 8.84 (1H) for **2**. Both signals were assigned to -CONH$_2$ protons of the coordinated salicylamidato ligand by the comparison with those (δ=7.5—8.7) of

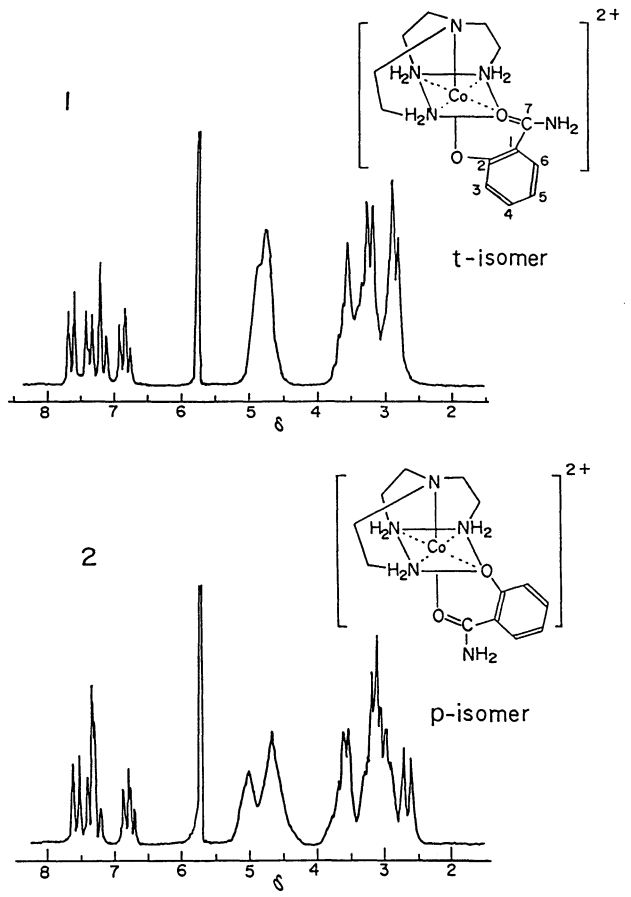


Fig. 2. ^{1}H NMR spectra of complexes **1** and **2** in 1.8 mol dm^{-3} D_2SO_4.
1: *t*-[Co(A)tren]$Cl_2 \cdot H_2O$. **2**: *p*-[Co(A)tren]$Cl_2 \cdot H_2O$.

free salicylamide.[14] Thus, complexes **1** and **2** have been assigned to **A**-type complexes, $[Co(A)tren]^{2+}$. On the other hand, the electric conductivities of **3** and **4** are ca. 110 S cm^2 mol^{-1}. The IR spectra of **3** and **4** do not show a band due to the C=O stretching vibration. Complexes **3** and **4** have been obtained from a reaction mixture (pH 10) of **1** and **2** with an ammonia solution, respectively (cf. Experimental section). Thus, complexes **3** and **4** have been assigned to **C**-type complexes, $[Co(C)tren]^+$. Complexes **3** and **4** are very slightly soluble in DMSO, though **1** and **2** are soluble. The chemical shifts of the C-1 carbon (position: cf. Fig. 2) signal for **3** and **4** are at a lower field than those of **1** and **2** (Table 1). The ε values of the charge-transfer band at ca. 340 nm in the absorption spectra for **3** and **4** are smaller than those of **1** and **2** (Table 1).

The electric conductivities of **5** and **6** are ca. 250 S cm^2 mol^{-1}. The IR spectra of **5** and **6** showed a band due to C=O stretching vibration at 1630—1644 cm^{-1}. The $-CONH_2$ proton signals of the coordinated salicylamidato ligand of **5** and **6** are observed in the region δ=8.6—9.0 in DMSO-d_6 (Fig. 3). Thus, complexes **5** and **6** are assigned to the **A**-type. The electric conductivity of **7** is 115 S cm^2 mol^{-1}. The IR spectrum of **7** does not show a band due to the C=O stretching vibration. Complex **7** is very slightly soluble in DMSO. Complex **7** was obtained from a reaction mixture (pH 10) of **5** and an ammonia solution. Thus, complex **7** is assigned to the **C**-type. Next, the electric conductivity of **9** is 145 S cm^2 mol^{-1}. The absorption spectrum of **9** shows split first bands at 510 and 535 nm. The

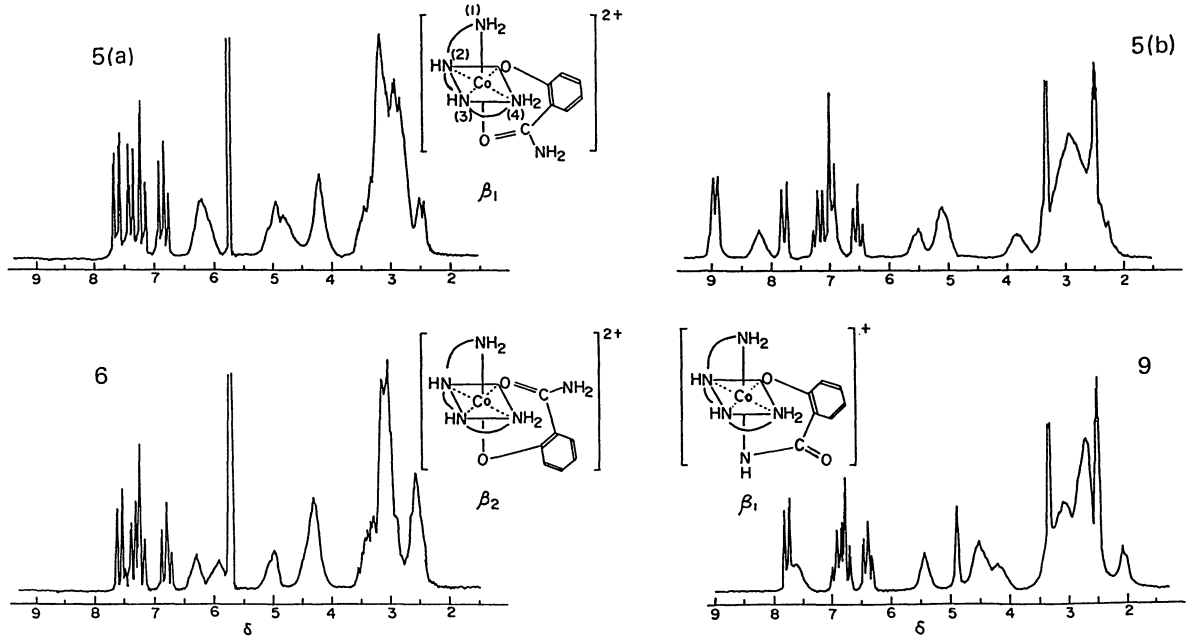


Fig. 3. ^{1}H NMR spectra of complexes **5**, **6**, and **9**.
5(a): *cis*-β_1-[Co(A)trien]$Cl_2 \cdot 2H_2O$ in 1.8 mol dm^{-3} D_2SO_4.
5(b): *cis*-β_1-[Co(A)trien]$Cl_2 \cdot 2H_2O$ in DMSO-d_6.
6: *cis*-β_2-[Co(A)trien]$Cl_2 \cdot 2H_2O$ in 1.8 mol dm^{-3} D_2SO_4.
9: *cis*-β_1-[Co(D)trien]$Cl \cdot H_2O$ in DMSO-d_6.

$-CONH^-$ proton signal of the coordinated salicylamidato ligand of **9** is observed at δ=4.89 in DMSO-d_6 (Fig. 3). The C-1 carbon signal of **9** is observed at δ=121.5. These properties of **9** are in agreement with those of **17**, which were reported previously (Table 1). Thus, complex **9** is assigned to the **D**-type, $[Co(\mathbf{D})(trien)]^+$.

The results of the electric conductivities, IR, ^1H, ^{13}C, and absorption spectra of **10**, **11**, and **12** are similar to those of (**1**, **2**, **5**, **6**), (**3**, **4**, **7**), and **9**, respectively, as shown in Table 1 and the Experimental section. Thus, **10**, **11**, and **12** are assigned to the **A**-, **C**-, and **D**-type complexes, respectively.

Isomers of the Complexes. Octahedral salicylamidato(tren)cobalt(III) complexes exist in the *t*- and *p*-isomeric forms[10,15] (Fig. 2). A distinction between **1** and **2** was found in the ^1H NMR spectra in 1.8 mol dm^{-3} D_2SO_4 (Fig. 2). The chemical shift (δ=4.69) of the proton signal of the NH_2 groups of the coordinated tren ligand of **2** is at a higher field than that (δ=4.75) of **1**, i.e., the NH_2 group of **2** is considered to be at a position trans to the phenoxyl oxygen of the coordinated salicylamidato ligand, which is more electronegative than the carbonyl oxygen.[10] Also, the signals of the methylene protons for **2** show two very sharp peaks[10] in the region δ=2.5—2.8; those for **1**, however, do not show the corresponding peaks (Fig. 2). These properties of **1** and **2** are similar to those of the corresponding complexes, **13** and **14**, respectively. Thus, **1** and **2** are assigned to the *t*- and *p*-isomers, respectively, as shown in Fig. 2. Next, the chemical shift (δ=4.85) of the proton signal of the NH_2 groups of the coordinated tren ligand of **4** in the ^1H NMR spectra in 1.8 mol dm^{-3} D_2SO_4 is at a higher field than that (δ=5.00) of **3**. The signals of the methylene protons of **4** show two very sharp peaks in the region δ=2.5—2.8, but those for **2** do not show the corresponding peaks (cf. Experimental section). In addition, complexes **3** and **4** were obtained from a reaction mixture (pH 10) of **1** and **2** with an ammonia solution, respectively. Thus, complexes **3** and **4** are assigned to the *t*- and *p*-isomers, respectively. No isomerization between *t*-isomer (**1**, **3**) and *p*-isomer (**2**, **4**) was observed in water and methanol at room temperature.

Octahedral salicylamidato(trien)cobalt(III) complexes exist in three geometrical isomers of *cis*-α, *cis*-β_1, and *cis*-β_2.[8,10] The IR spectra of **5**—**7** and **9** show 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}) (cf. Experimental section). The ^{13}C NMR spectra of **5**—**7** and **9** show six carbon signals for the coordinated trien ligand. Thus, complexes **5**—**7** and **9** are assigned to the *cis*-β-form.[5,8] A distinction between **5** and **6** was observed in the ^1H NMR spectra in 1.8 mol dm^{-3} D_2SO_4 and the absorption spectra: the methylene proton signals of **6** were divided into two groups at δ=2.3—2.8 (3H) and 2.8—3.7 (9H) (Fig. 3); those of **5** could not be divided. The ε value of the first absorption band of **5** is greater than that of **6**. These properties for **5** and **6** are similar to those of **15** and **16**, respectively. Thus, complexes **5** and **6** were assigned to the *cis*-β_1 and β_2-isomers, respectively, as shown in Fig. 3. No isomerization between **5** and **6** was observed in water at room temperature. The methylene proton signals of **7** in 1.8 mol dm^{-3} D_2SO_4 are very close to those of **5**. Complex **7** was obtained directly from a reaction mixture (pH 10) of **5** and an ammonia solution. Thus, complex **7** was assigned to the *cis*-β_1-isomer. On the other hand, complex **7** and another complex **8** were obtained from a reaction mixture (pH 10) of **6** and an ammonia solution. Complex **8** could be assigned to the *cis*-β_2-isomer, but could not be isolated from the reaction mixture by the chromatographic method, because **8** isomerized to **7**. The methylene proton signals of **9** in 1.8 mol dm^{-3} D_2SO_4 are very close to those of **5** and **7**. Thus, complex **9** can be assigned to the *cis*-β_1-isomer.

In this study, **A**-, **C**-, and **D**-type complexes have been prepared. The formation of the **A**-type complexes is due to the bond between a cobalt atom and carbonyl oxygen of salicylamide ligand. The **C**-type complexes have been formed by the deprotonation of $-CONH_2$ of the coordinated salicylamidato ligand of the **A**-type complexes, since the **C**-type complexes have been obtained from a reaction mixture (pH 10) of the **A**-type complexes and an ammonia solution. The formation of the **D**-type complexes is due to the bond between a cobalt atom and the deprotonated imide nitrogen ($-CONH^-$) from $-CONH_2$ of the salicylamide ligand in an alkaline solution.

The different properties between the **A**-type complexes and the **C**- and **D**-type complexes are as follows: i) Yield (30—50%) of the **A**-type complexes was larger than those (4—9% for **C** and 2—3% for **D**) of the **C**- and **D**-type complexes at pH 8.6, but that (20%) of the **A**-type complexes decreases at pH 10 and those (15% for **C** and 3—5% for **D**) of the **C**- and **D**-type complexes increase. Thus, the preparation of the mixed-ligand cobalt(III) complexes with the salicylamidato ligand has been dependent upon the pH of the reaction mixture. ii) The chemical shifts (δ=113—115) of the C-1 carbon signals for the **A**-type complexes are at a higher field than those (δ=117—122) of the **C**- and **D**-type complexes. iii) The ε values (3400—3700) of the charge-transfer band at ca. 340 nm in the absorption spectra for the **A**-type complexes are greater than those (2500—3000) of the **C**- and **D**-type complexes.

The **C**-type and **D**-type complexes are a linkage isomer. A characteristic property of this linkage isomer has been observed in the absorption and ^{13}C NMR spectra as well as solubility in DMSO: i.e., the first absorption band for the **D**-type complexes shows split first bands at ca. 510 and 535 nm; that for the **C**-type complexes, however, does not show a split first band. The C-1 carbon signals of the **D**-type complexes are observed in the region δ=120—122, but those of the **C**-type complexes are observed at δ=117—118. The **D**-

type complexes are soluble in DMSO, but the **C**-type complexes are very slightly soluble.

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