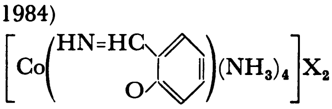
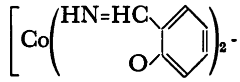
2650 © *1984 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, *57*, *2650—2656 (1984)* [Vol. 57, No. 9

Cobalt(III) Complexes with [$N_{6-n}X_n$] type Ligands. IV.[1] The Preparation and Properties of Tetraammine(salicylideneaminato)cobalt(III) and Diamminebis(salicylideneaminato)cobalt(III) Complexes

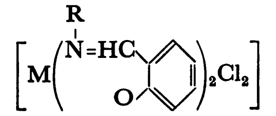
Yoshihisa Yamamoto* and Eiko Toyota
Faculty of Pharmaceutical Sciences, Higashi Nippon Gakuen University, Ishikari-Tobetsu, Hokkaido 061-02

(Received Febuary 14, 1984)

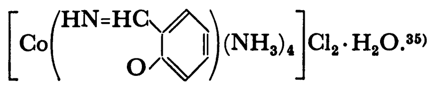
Tetraammine(salicylideneaminato)cobalt(III) complexes,  (X: Cl, NO_3, ClO_4, and picrate) and diamminebis(salicylideneaminato)cobalt(III) complexes,  $(NH_3)_2$]$X\cdot nH_2O$ (X: Cl, NO_3, ClO_4, and picrate), have been isolated from a reaction mixture of $CoCl_2\cdot 6H_2O$, 25% aqueous ammonia, 30% H_2O_2 and salicylaldehyde, and characterized. In the latter complexes, the three isomers of green, orange and brown color have been isolated by column chromatography on alumina and their configurations have been established by their NMR spectra, *i.e.*, the configuration of the green complex is in the *trans-trans-trans* positions for two ammine ligands, and two phenoxyl groups and two CH=NH groups of the coordinated salicylideneaminato ligands, respectively, while those of the orange and brown complexes are in the *trans-cis-cis* and *cis-cis-trans* positions, respectively.

Previously, we have been concerned with the preparation, properties and isomers of the mixed ligand complexes of the [$CoN_{6-n}O_n$] type, *e.g*, salicylato(amine)cobalt(III) complexes,[2–7] [Co(sal-R)L]$X\cdot nH_2O$, and amine(8-quinolinolato)cobalt(III) complexes,[8–12] [$Co(oxine\text{-}R)_lL$]$X_m\cdot nH_2O$, (L: NH_3, en, bpy, trien, 2,3,2-tet, 3,2,3-tet, and 3,3,3-tet; R: H, Me; *l*: 1 or 2; *m*: 1 or 2). The *cis*-β_1 and β_2 isomers of salicylato(quadridentate amine)cobalt(III) complexes have been isolated and the ^1H and ^{13}C chemical shifts of their amine protons, methylene protons and methylene carbons have been assigned. In addition, the configurations of the coordinated two (2-methyl-)8-quinolinolato ligands in ethylenediaminebis(2-methyl-8-quinolinolato)cobalt(III) complexes[8] and diamminebis(8-quinolinolato)cobalt(III) complexes[10,11] have been reported. The former of these complexes has a *cis-trans* configuration for the two oxygen and two nitrogen atoms, and the latter has a *trans-cis* configuration for the two oxygen and two nitrogen atoms.

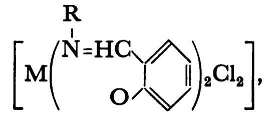
Many investigations of bis- or tris(*N*-substituted salicylideneaminato)metal complexes have been reported especially concerning the preparation,[13–28] geometrical isomerism,[28–30] IR spectra,[14–16] absorption spectra,[14–23] NMR spectra,[14,29] and magnetic susceptibilities.[15–19,24,25] However the isolation and stereochemistry of the mixed ligand metal complexes with salicylideneaminato ligand and the derivatives in an octahedral configuration have not previously been described except for dichlorobis(*N*-substituted salicylideneaminato) metal,



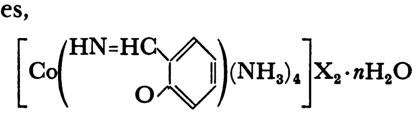
(M: Ti,[31] Mo,[32] Sn,[33] and Th[34]), and tetraammine(salicylideneaminato)cobalt(III) complexes,

 [35]

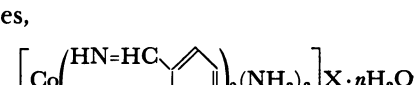
In the stereochemistry of

,

the configuration of the coordinated *N*-substituted salicylideneaminato ligands is *trans-trans* for the two phenoxyl and two CH=NR groups. However, other isomers with *cis-trans* configurations and *cis-cis* configurations for the two phenoxyl and two CH=NR groups of the coordinated salicylideneaminato ligand and the *N*-substituted derivatives have not yet been reported. The present paper deals with the preparation and properties of the mixed ligand complexes with salicylideneaminato and ammine ligands of tetraammine(salicylideneaminato)cobalt(III) complexes,



and diamminebis(salicylideneaminato)cobalt(III) complexes,

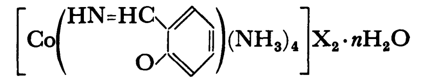


(X: Cl, NO_3, ClO_4, pic), and deals with the assignment of the configuration of the latter complexes.

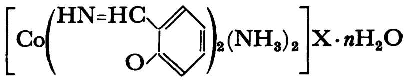
Results and Discussion

The abbreviations of the ammine(salicylideneaminato)cobalt(III) complexes studied in this research are listed in Table 1. Russet tetraammine(salicylideneaminato)cobalt(III) chloride hydrate,

Table 1. The abbreviations of the ammine(salicylideneaminato)cobalt(III) complexes



1a—d



2a—d, 3a—d, 4a—d

	1a	1b	1c	1d	2a	2b	2c	2d	3a	3b	3c	3d	4a	4b	4c	4d
X	Cl	NO_3	ClO_4	pic	Cl	NO_3	ClO_4	pic	Cl	NO_3	ClO_4	pic	Cl	NO_3	ClO_4	pic
n	1	0	0	0	1	1	0	0	1	2	0	0		1	0	0
Form					*trans*—*trans*—*trans* NH_3—O—CH=NH				*trans*—*cis*—*cis* NH_3—O—CH=NH				*cis*—*cis*—*trans* NH_3—O—CH=NH			

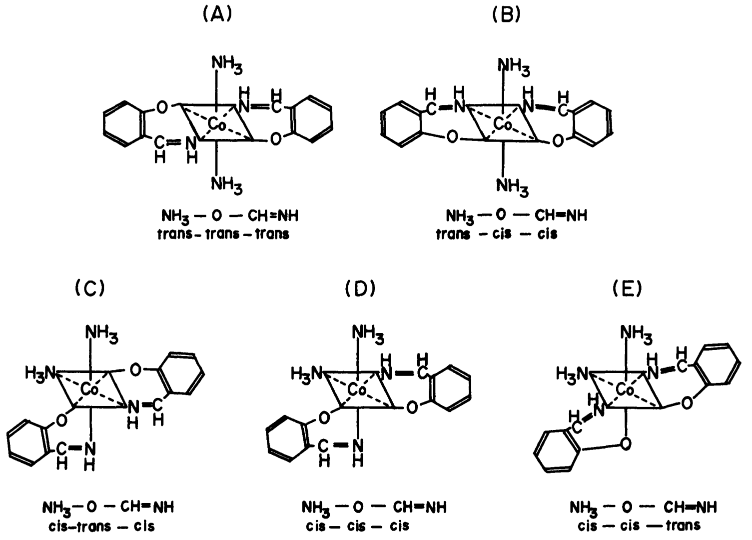
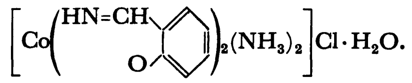
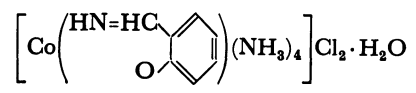
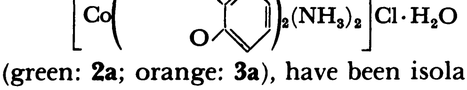


Fig. 1. The configurations of 



(**1a**), and green and orange diamminebis(salicylideneaminato)cobalt(III) chloride hydrate,

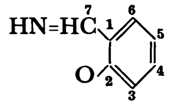


(green: **2a**; orange: **3a**), have been isolated by column chromatography on alumina from a reaction mixture of $CoCl_2\cdot 6H_2O$, 25% aqueous ammonia, 30% H_2O_2 and salicylaldehyde. Brown diamminebis(salicylideneaminato)cobalt(III) nitrate hydrate (**4b**) has been isolated by chromatography on alumina from a reaction mixture of **2a** and silver nitrate, while the corresponding chloride (**4a**) could not be isolated on the solid state (*cf*. Experimental section). The corresponding nitrates (**1b**, **2b**, **3b**), perchlorates (**1c**, **2c**, **3c**, **4c**) and picrates (**1d**, **2d**, **3d**, **4d**) have been prepared from a reaction mixture of **1a**, **2a**, **3a**, or **4b** and silver nitrate, sodium perchlorate, or picric acid, respectively. The diamminebis(salicylideneaminato)cobalt(III) complex has five possible isomers of A, B, C, D, and E as is shown in Fig. 1. The configurations of isomers A, B, C, and E have C_2 symmetry, while isomer D has C_i symmetry.

The electric conductivities of **1a**—**c** in aqueous solutions were 190—220 S cm^2 equiv^{-1} and those of **2a**—**c**, **3a**—**c** and **4b**—**c** were 100—110 S cm^2 equiv^{-1} as is shown in the experimental section. In the IR spectra, bands due to the C=N streching vibrations[14–16,31,33,34] and rocking deformation vibrations[36–38] of all complexes were observed at 1625 cm^{-1} and in the 810—830 cm^{-1} regions, respectively (*cf*. Experimental section). These complexes are diamagnetic complexes of low spin type from their magnetic susceptibilities. In the absorption spectra of **1a**—**c**, **2a**—**c**, **3a**—**c**, and **4b**—**c** in methanol, the absorption bands at about 380 nm are assigned to the charge transfer band[10,11] and those at about 540 nm or 610 nm are the first absorption bands as shown in Table 2. The ε values at about 380 nm of **2a**—**c**, **3a**—**c**, and **4b**—**c** are larger than those of **1a**—**c** as shown in Table 2.

The ^{1}H NMR spectra of all complexes were measured in DMSO-d_6 and the ^{13}C NMR spectra of **1a**, **2a**, **3a**, and **4b** were measured in D_2O and 14% ammonia-D_2O solution as shown in Fig. 2. The ^{1}H and ^{13}C NMR spectra of **2a**—**d**, **3a**—**d**, and **4b**—**d** are consistent with C_2 symmetry.[8,11,39,40] In the ^{1}H NMR spectra, the signals at 2.6—4.1 ppm of these complexes are assigned to the protons of the coordinated ammine ligands. The multiplet signals at 6.4—7.3 ppm are assigned to the ring protons of the coordinated salicylideneaminato ligand (abbreviation: the

Table 2. ^1H NMR spectra and absorption bands of **1a—d**, **2a—d**, **3a—d**, and **4a—d** complexes



No	NH_3 δ			δ					Absorption bands in methanol λ/nm (ε)		
	$N(1)H_3$ $N(4)H_3$	$N(2)H_3$ $[N(1)H_3+N(2)H_3]$	$N(3)H_3$	ring protons	CH=N	$^3J_{HCNH}$ Hz	C=NH	Picrate δ			
1a	3.26(s 6H)	3.46(s 3H)	4.07(s 3H)	6.43—7.30(m 4H)	8.00(d 1H)	10.5	11.08(d 1H)$^{1)}$		378(2750)	475 sh(185)	550(110)
1b	3.07(s 6H)	2.89(s 3H)	3.81(s 3H)	6.47—7.32(m 4H)	8.03(d 1H)	10.5	10.48(d 1H)$^{1)}$		378(2820)	475 sh(185)	550(110)
1c	3.03(s 6H)	2.78(s 3H)	3.76(s 3H)	6.48—7.33(m 4H)	8.03(d 1H)	10.5	10.48(d 1H)$^{1)}$		378(2880)	475 sh(185)	550(110)
1d	3.09(s 6H)	2.85(s 3H)	3.82(s 3H)	6.51—7.37(m 4H)	8.08(d 1H)	10.5	10.57(d 1H)	8.55(s 4H)$^{1)}$			
2a		[2.60(s 6H)]		6.44—7.36(m 8H)	8.27(d 2H)	11.2	11.16(d 2H)$^{1)}$		383(4850)		610(85)
2b		[2.59(s 6H)]		6.43—7.34(m 8H)	8.27(d 2H)	11.2	11.17(d 2H)$^{1)}$		385(4760)		605(85)
2c		[2.58(s 6H)]		6.43—7.34(m 8H)	8.25(d 2H)	11.2	11.15(d 2H)$^{1)}$		385(4640)		610(85)
2d		[2.60(s 6H)]		6.45—7.36(m 8H)	8.29(d 2H)	11.2	11.17(d 2H)	8.54(s 2H)$^{1)}$			
3a		[2.68(s 6H)]		6.43—7.37(m 8H)	7.87(d 2H)	10.5	10.59(d 2H)$^{1)}$		384(5070)	480 sh(415)	538(200)
3b		[2.72(s 6H)]		6.45—7.37(m 8H)	7.90(d 2H)	10.5	9.98(d 2H)$^{1)}$		384(4850)	480 sh(420)	538(200)
3c		[2.73(s 6H)]		6.43—7.33(m 8H)	7.88(d 2H)	10.5	9.99(d 2H)$^{1)}$		383(5140)	480 sh(400)	538(200)
3d		[2.73(s 6H)]		6.46—7.37(m 8H)	7.92(d 2H)	10.5	10.02(d 2H)	8.52(s 2H)$^{1)}$			
4a$^{a)}$		[3.51(s)]		6.44—7.27(m)	7.75(d)	10.5	10.27(d)$^{1)}$				
4b		[3.49(s 6H)]		6.42—7.26(m 8H)	7.72(d 2H)	10.5	10.26(d 2H)$^{1)}$		380(4650)		530(280)
4c		[3.47(s 6H)]		6.44—7.29(m 8H)	7.74(d 2H)	10.5	10.27(d 2H)$^{1)}$		380(4500)		530(280)
4d		[3.48(s 6H)]		6.44—7.28(m 8H)	7.74(d 2H)	10.5	10.27(d 2H)	8.50(s 2H)$^{1)}$			

Solvent and standard: 1) DMSO-d_6, internal TMS ($\delta=0$). a): Experimental section.

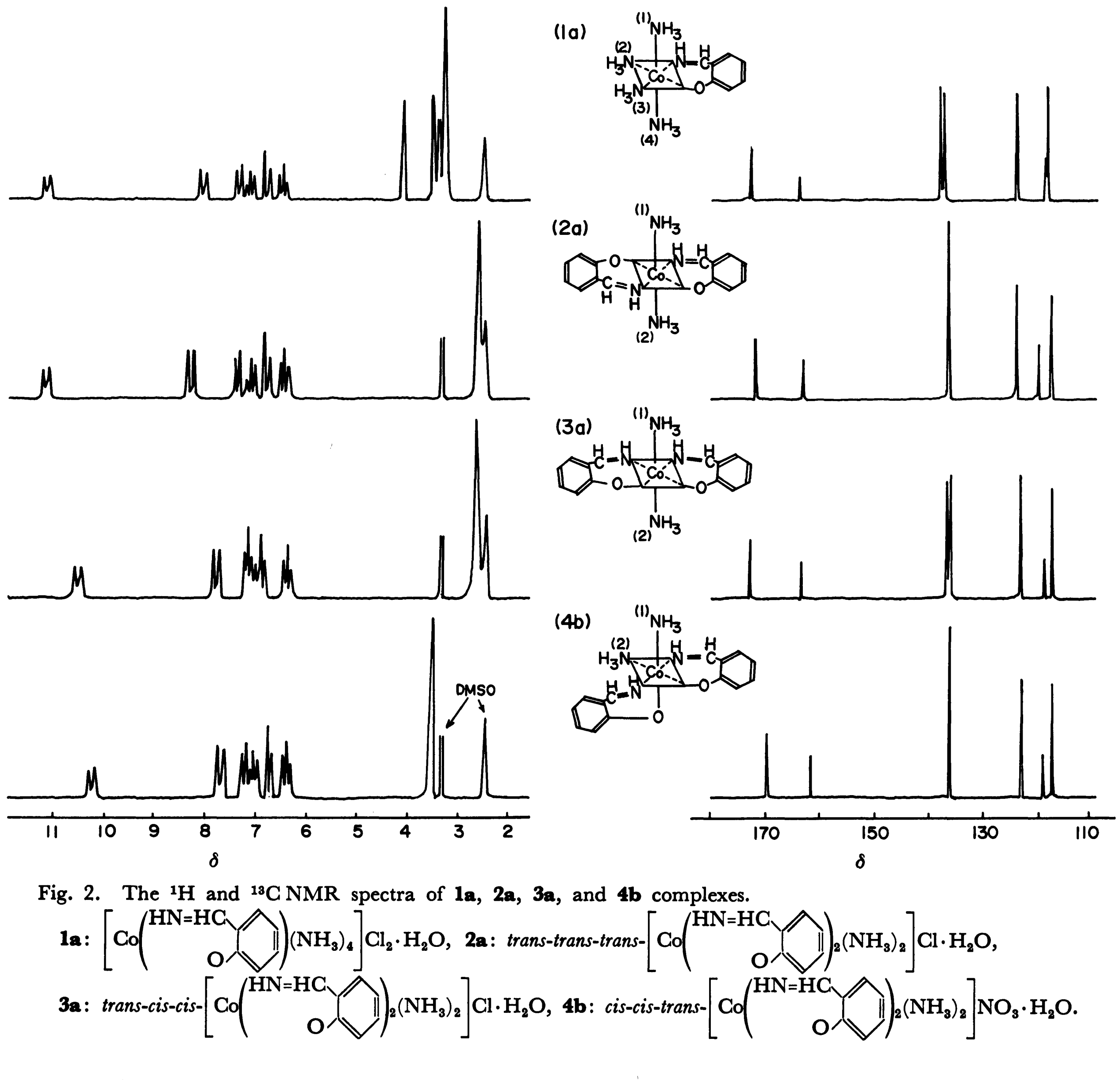
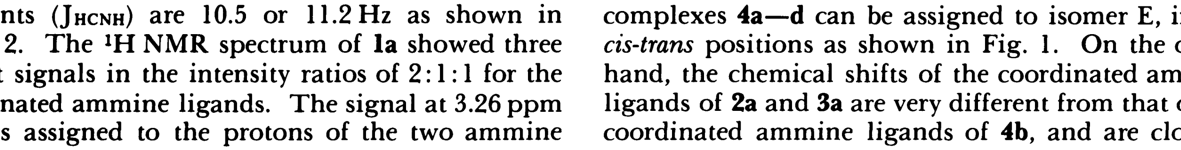
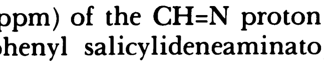


Fig. 2. The ^{1}H and ^{13}C NMR spectra of **1a**, **2a**, **3a**, and **4b** complexes.



chelate ligand). The doublet signal at about 8 ppm can be assigned to the CH=N proton.[29,33,34] The doublet signal at 10—11 ppm can be assigned to the C=NH proton of the chelate ligand. Their coupling constants (J_{HCNH}) are 10.5 or 11.2 Hz as shown in Table 2. The ^{1}H NMR spectrum of **1a** showed three singlet signals in the intensity ratios of 2:1:1 for the coordinated ammine ligands. The signal at 3.26 ppm (6H) is assigned to the protons of the two ammine ligands of N(1)H$_3$ and N(4)H$_3$ in the positions *cis* to the coordinated chelate ligand, because the two ammine ligands should be equivalent.[11] The singlets at 3.46 ppm (3H) and at 4.07 ppm (3H) are assigned to the protons of the ammine ligands of N(2)H$_3$ and N(3)H$_3$ in the position trans[6,11,41] of the phenoxyl and CH=NH group of the coordinated chelate ligand, respectively. The signals of the ammine protons and the C=NH proton of **1a** are at a lower field than those of **1b—d**.

The signal at 3.49 ppm of **4b** is similar to that (3.46 ppm, 3H) of N(2)H$_3$ of **1a**, and thus the signal of **4b** can be assigned to the ammine protons in the *trans* positions of the phenoxyl groups of the coordinated chelate ligands. Thus, the configuration of complexes **4a—d** can be assigned to isomer E, in *cis-cis-trans* positions as shown in Fig. 1. On the other hand, the chemical shifts of the coordinated ammine ligands of **2a** and **3a** are very different from that of the coordinated ammine ligands of **4b**, and are close to that of N(1)H$_3$ and N(4)H$_3$ in the *trans* positions of **1a**. Accordingly the ammine proton signals of **2a** and **3a** can be assigned to those in the *trans* position to each other. A clear distinction between complexes **2a** and **3a** was found in the CH=NH proton signals of their ^{1}H NMR spectra as shown in Fig. 2. The CH=NH proton signals of **2a** are at a lower field than those of **3a**. Thus, the configuration of the two CH=NH groups of the coordinated chelate ligands of **2a** is *trans*[6,10,41] because the nitrogen atom of CH=NH group is less electronegative than the oxygen atom of the phenoxyl group. In addition, the chemical shift (8.27 ppm) of the CH=N proton signal of **2a** is similar to that[34] (8.5 ppm) of the CH=N proton signal of dichlorobis(*N*-phenyl salicylideneaminato)thorium complex,



(**5**). This is *trans-trans-trans* for the two chloro ligands, the two phenoxyl groups and the two CH=N(Ph) groups of the coordinated chelate ligands, respectively. Accordingly the configuration of **2a** has been assigned to isomer A, which is *trans-trans-trans* and that of **3a** has been assigned to isomer B which is *trans-cis-cis* as shown in Fig. 1.

The ^{13}C NMR spectra of **1a**, **2a**, **3a**, and **4b** showed seven signals for the chelated ligand as shown in Fig. 2. Their chemical shifts were assigned on the basis of the results of those of salicylaldehyde[42] and tetraammine(salicylato)cobalt(III) chloride hydrate.[6] The ^{13}C NMR results, color, decomposition temperature of the complexes are collected in the experimental section.

Experimental

Measurements. The NMR spectra were recorded with an FX-60 apparatus (JEOL) for ^{13}C NMR and with an R-40 apparatus (Hitachi) for ^{1}H NMR. The IR spectra were recorded as potassium bromide disks with an IR-27G apparatus (Shimadzu). The visible absorption spectra were recorded with a Shimadzu MPS-5000 recording spectrophotometer. The electric conductivities of the aqueous solutions were determined by the use of a conductometric meter CM-30 (Shimadzu) at room temperature. The magnetic susceptibilities were measured by the Faraday method using a magnetic balance (Shimadzu) at room temperature.

*Preparation of Complexes. Tetraammine(salicylideneaminato)cobalt(III) Chloride Hydrate (**1a**), Diamminebis(salicylideneaminato)cobalt(III) Chloride Hydrate (**2a** and **3a**) and Hexaamminecobalt(III) Chloride (**6**)*: A 25% aqueous ammonia (40 cm^3) was added to an aqueous solution (20 cm^3) of $CoCl_2 \cdot 6H_2O$ (10.0 g, 42.0 mmol), and about 5 cm^3 of 30% H_2O_2 solution was added slowly to the solution at 0 °C. The color of the solution changed from brown to red. A methanol solution (50 cm^3) of salicylaldehyde (5.13 g, 42.0 mmol) was added dropwise to the solution during 2 h at 50 °C. The solution was stirred for 1 d at 50 °C, concentrated with a rotary evaporator at 50 °C, and dried over silica gel. Complexes **1a**, **2a**, and **3a** were extracted with 200 cm^3 of dry methanol from the dried reaction mixture. The methanol solution was concentrated to about 50 cm^3 with a rotary evaporator at 50 °C, the complex **1a** precipitated was filtered and recrystallized twice from water–ethanol. The separation of complexes **2a** and **3a** from the filtrate was achieved by column chromatography on alumina. On elution with methanol, the effluent of the first green band (complex **2a**) was collected, concentrated and recrystallized from 10% aqueous ammonia twice. The effluent of the second orange band (complex **3a**) was collected, concentrated and recrystallized twice from water. The russet band of complex **1a** in the filtrate moved only slightly on alumina. Complex **6** which remained was not soluble in dry methanol. Complex **2a** isomerizes to **4a** at 20 °C in DMSO, methanol and water, but the isomerization is very slow in 10% aqueous ammonia at 20 °C. Yields: 3.6 g (25.5%) for **1a**; 2.8 g (17.2%) for **2a**; 0.65 g (4.0%) for **3a**; 3.59 g (32%) for **6**. Found **1a**: C, 25.26; H, 6.34; N, 20.66; Cl, 21.57%. **2a**: C, 43.98; H, 5.17; N, 14.16; Cl, 9.77%. **3a**: C, 43.55; H, 5.66; N, 14.12; Cl, 9.57%. Calcd for **1a**: $CoC_7H_{20}N_5O_2Cl_2$ (MW 336.11) C, 25.01; H, 6.00; N, 20.84; Cl, 21.10%. **2a** and **3a**: $CoC_{14}H_{20}N_4O_3Cl$ (MW 386.73) C, 43.48; H, 5.21; N, 14.49; Cl, 9.17%. Color **1a**: russet; **2a**: green; **3a**: orange. Dp: 161—163 °C for **1a**; 195—197 °C for **2a**; 163—165 °C for **3a**. Λ=220 for **1a**, 104 for **2a**, and 102 S cm^2 equiv^{-1} for **3a** in water. IR spectra: 1625 cm^{-1} (C=N), 810 cm^{-1} ($\rho_r(NH_3)_r$) for **1a** and **2a**: 1625 cm^{-1} (C=N), 825 cm^{-1} ($\rho_r(NH_3)_r$) for **3a**. ^{13}C NMR spectra: δ 117.9(c-1)*, 163.2(c-2), 117.5(c-3), 137.0(c-4), 123.1(c-5), 136.3 (c-6), 173.0(c-7) in D_2O. **2a**: δ 119.3(c-1), 163.5(c-2), 117.1 (c-3), 136.2(c-4), 123.4(c-5), 136.2(c-6), 172.6(c-7) in 14% ammonia-D_2O. **3a**: δ 118.6(c-1), 163.0(c-2), 117.0(c-3), 137.0 (c-4), 123.1(c-5), 136.2(c-6), 174.2(c-7) in D_2O.

*Brown Diamminebis(salicylideneaminato)cobalt(III) Chloride (**4a**)*: Complex **4a** was identified by the isomerization of **2a** in DMSO, methanol and water. A brown band of **4a** and a green band of **2a** are separated by column chromatography on alumina from a methanol solution of **2a**. From a brown solution, complex **2a** was obtained, complex **4a** could not be obtained in the solid state. The ^{1}H NMR spectrum of **4a** was observed in DMSO solution of **2a** at room temperature.

*Tetraammine(salicylideneaminato)cobalt(III) Nitrate (**1b**)*: An aqueous solution of silver nitrate (4.04 g, 23.8 mmol) was added to an aqueous solution of **1a** (4.0 g, 11.9 mmol), the mixture was stirred, and the precipitated silver chloride was filtered. The filtrate was concentrated and recrystallized from water twice. Yield: 3.6 g (81.5%). Found: C, 22.24; H, 4.74; N, 26.09%. Calcd for $CoC_7H_{18}N_7O_7$ (MW 371.20) C, 22.65; H, 4.89; N, 26.41%. Color: reddish brown. Dp: 147—148 °C. Λ=215 S cm^2 equiv^{-1} in water. IR spectrum: 1625 cm^{-1} (C=N), 810 cm^{-1} ($\rho_r(NH_3)_r$).

*Tetraammine(salicylideneaminato)cobalt(III) Perchlorate (**1c**)*: An aqueous solution of sodium perchlorate (2.2 g, 18.0 mmol) was added to an aqueous solution of **1a** (3.0 g, 8.9 mmol), the mixture was stirred for 1 h at 40 °C, and was concentrated with a rotary evaporator and dried. Complex **1c** was extracted with 15 cm^3 of acetone from the dried reaction mixture. The acetone solution was concentrated and recrystallized from water twice. Yield: 3.0 g (75.6%). Found: C, 19.04; H, 4.50; N, 15.78; Cl, 16.13%. Calcd for $CoC_7H_{18}N_5O_9Cl_2$ (MW 446.09) C, 18.85; H, 4.07; N, 15.70; Cl, 15.89%. Color: reddish brown. Dp: 212—215 °C. Λ=191 S cm^2 equiv^{-1} in water. IR spectrum: 1625 cm^{-1} (C=N), 810 cm^{-1} ($\rho_r(NH_3)_r$).

*Tetraammine(salicylideneaminato)cobalt(III) Picrate (**1d**)*: An aqueous solution of **1a** (0.5 g, 1.49 mmol) was added to an aqueous solution of picric acid (0.68 g, 2.97 mmol), the mixture was stirred. The complex **1d** was precipitated, filtered, washed with water and dried. Yield: 0.18 g (77.3%). Found: C, 32.67; H, 3.06; N, 21.73%. Calcd for $CoC_{19}H_{22}N_{11}O_{15}$ (MW 703.39) C, 32.44; H, 3.15; N, 21.90%. Color: yellowish brown. Dp: 185—187 °C. IR spectrum: 1625 cm^{-1} (C=N), 810 cm^{-1} ($\rho_r(NH_3)_r$).

trans-trans-trans *and* cis-cis-trans-*Diamminebis(salicylideneaminato)cobalt(III) Nitrate Hydrate (**2b** and **4b**)*: An aqueous solution of silver nitrate (1.1 g, 6.48 mmol) was added to a methanol–water (1:1) solution of **2a** (2.5 g, 6.46 mmol), the mixture was stirred, and the precipitated silver chloride was filtered. The filtrate was concentrated and the complexes **2b** and **4b** were separated by column chromatography on alumina. On elution with methanol, the effluent of the first green band (**2b**) was collected and concentrated and recrystallized from methanol–ether twice. The effluent of the second brown band (**4b**) was collected, concentrated and recrystallized from methanol-ether twice. Yields: 0.85 g

---

*: position: Table 2.

(31.8%) for **2b** and 0.96 g (36.0%) for **4b**. Found **2b**: C, 40.94; H, 4.56; N, 17.25%. **4b**: C, 40.24; H, 4.49; N, 17.10%. Calcd for $CoC_{14}H_{20}N_5O_6$ (MW 413.28) C, 40.69; H, 4.88; N, 16.95%. Color **2b**: greenish brown; **4b**: brown. Dp: 186—188 °C for **2b**; 183—185 °C for **4b**. Λ=108 for **2b**, 105 S cm^2 equiv^{-1} for **4b** in water. IR spectra: 1625 cm^{-1} (C=N), 820 cm^{-1} (ρ_r(NH$_3$)$_r$) for **2b**; 1625 cm^{-1} (C=N), 830 cm^{-1} (ρ_r(NH$_3$)$_r$) for **4b**. ^{13}C NMR spectrum **4b**: δ 119.0(c-1), 162.8(c-2), 117.2 (c-3), 136.2(c-4), 122.7(c-5), 136.2(c-6), 170.8(c-7) in D_2O.

trans-cis-cis-*Diamminebis(salicylideneaminato)cobalt(III) Nitrate Dihydrate (3b)*: This complex was prepared from the reaction mixture of silver nitrate (0.22 g, 1.30 mmol) and **3a** (0.5 g, 1.29 mmol). The mixture was stirred, and the silver chloride precipitate filtered. The filtrate was concentrated on a rotary evaporator. A small amount of silver complex in the filtrate was excluded by column chromatography on alumina. Complex **3b** was recrystallized from methanol-ether twice. Yield: 0.37 g (66.5%). Found: C, 38.77; H, 5.30; N, 16.55%. Calcd for $CoC_{14}H_{22}N_5O_7$ (NW 431.30) C, 38.99; H, 5.14; N, 16.24%. Color: orange. Dp: 180-182 °C. Λ=107 S cm^2 equiv^{-1} in water. IR spectrum: 1625 cm^{-1} (C=N), 830 cm^{-1} (ρ_r(NH$_3$)$_r$).

trans-trans-trans *and* trans-cis-cis-*Diamminebis(salicylideneaminato)cobalt(III) Perchlorate (2c and 3c)*: An aqueous solution of sodium perchlorate (0.16 g, 1.31 mmol) was added to a methanol-water (1:1) solution of **2a** or **3a** (0.5 g, 1.29 mmol), and the precipitated complex **2c** or **3c** was filtered, and washed with ethanol-ether. Yields: 0.53 g (94.9%) for **2c**, 0.51 g (91.4%) for **3c**. Found **2c**: C, 38.90; H, 4.17; N, 12.76; Cl, 8.65%. **3c**: C, 38.61; H, 4.22; N, 12.43; Cl, 7.90%. Calcd for $CoC_{14}H_{18}N_4O_6Cl$ (MW 432.71) C, 38.86; H, 4.19; N, 12.95; Cl, 8.19%. Color **2c**: green; **3c**: orange. Dp: 225—226 °C for **2c**; 225—227 °C for **3c**. Λ=112 for **2c**, 106 S cm^2 equiv^{-1} for **3c** in water. IR spectra: 1625 cm^{-1} (C=N), 810 cm^{-1} (ρ_r(NH$_3$)$_r$) for **2c**; 1625 cm^{-1} (C=N), 830 cm^{-1} (ρ_r(NH$_3$)$_r$) for **3c**.

cis-cis-trans-*Diamminebis(salicylideneaminato)cobalt(III) Perchlorate (4c)*: This complex was prepared from the reaction mixture of sodium perchlorate (0.1 g, 0.82 mmol) and **4b** (0.34 g, 0.82 mmol) according to the method of **1c**, and recrystallized from methanol-ether. Yield: 0.15 g (42.3%). Found: C, 38.73; H, 4.16; N, 12.76; Cl, 8.76%. Calcd for $CoC_{14}H_{18}N_4O_6Cl$ (MW 432.71) C, 38.86; H, 4.19; N, 12.95; Cl, 8.19%. Color: brown. Dp: 197—199 °C. Λ=103 S cm^2 equiv^{-1} in water. IR spectrum: 1625 cm^{-1} (C=N), 830 cm^{-1} (ρ_r(NH$_3$)$_r$).

trans-trans-trans, trans-cis-cis *and* cis-cis-trans-*Diamminebis(salicylideneaminato)cobalt(III) Picrate (2d, 3d, and 4d)*: These complexes were prepared from the reaction mixture of picraic acid (0.3 g, 1.31 mmol) and **2a** or **3a** (0.5 g, 1.29 mmol) or **4b** (0.54 g, 1.31 mmol) according to the method of **1d** Yields: 0.69 g (95.3%) for **2d**, 0.63 g (87.0%) for **3d**, 0.57 g (77.6%) for **4d**. Found **2d**: C, 42.10; H, 4.08; N, 17.15%. **3d**: C, 42.39; H, 3.81; N, 17.11%. **4d**: C, 42.51; H, 3.55; N, 17.11%. Calcd for $CoC_{20}H_{20}N_7O_9$ (MW 561.36) C, 42.79; H, 3.59; N, 17.47%. Color **2d** and **3d**: yellowish brown, **4d**: orange. Dp: 184—185 °C or **2d**, 193—194 °C for **3d**, 171—172 °C for **4d**. IR spectra: 1625 cm^{-1} (C=N), 820 cm^{-1} (ρ_r(NH$_3$)$_r$) for **2d**, 1625 cm^{-1} (C=N), 830 cm^{-1} (ρ_r(NH$_3$)$_r$) for **3d**; 1625 cm^{-1} (C=N), 825 cm^{-1} (ρ_r(NH$_3$)$_r$) for **4d**.

Solubility: Complexes **1a—c** are readily soluble in water and DMSO, and soluble in methanol and DMF, though insoluble in the other common organic solvents. Complex **1c** is soluble in acetone. Complex **1d** is soluble in DMSO, DMF and acetone, and somewhat soluble in methanol, and insoluble in water. Complexes **2a—d**, **3a—d**, and **4b—d** are soluble in DMSO. Complexes **2c—d**, **3c—d**, and **4c—d** are soluble in acetone. Complexes **2a—b**, **3a**, and **4b** are soluble in water, though **2c**, **3b—c**, and **4c** are slightly soluble, and **2d**, **3d**, and **4d** are insoluble in water. Complexes **2a—c**, **3b—c**, and **4b—c** are soluble in methanol, though **2d** and **3a** are somewhat soluble in methanol.

References

1) Part III: Ref. 8.

2) Y. Yamamoto, H. Kudo, and E. Toyota, *Bull. Chem. Soc. Jpn.*, **56**, 1051 (1983).

3) Y. Yamamoto, E. Toyota, and N. Mitsudera, *Bull. Chem. Soc. Jpn.*, **53**, 3517 (1980).

4) Y. Yamamoto and E. Toyota, *Bull. Chem. Soc. Jpn.*, **52**, 2540 (1979).

5) Y. Yamamoto and E. Toyota, *Chem. Pharm. Bull.*, **26**, 2275 (1978).

6) Y. Yamamoto, *Bull. Chem. Soc. Jpn.*, **51**, 2894 (1978).

7) Y. Yamamoto, M. Mori, H. Yoneda, S. Misumi, and K. Ito, *Bull. Chem. Soc. Jpn.*, **42**, 984 (1969).

8) Y. Yamamoto and E. Toyota, *Bull. Chem. Soc. Jpn.*, **57**, 47 (1984).

9) Y. Yamamoto, E. Toyota, and Y. Yamamoto, *Bull. Chem. Soc. Jpn.*, **56**, 2721 (1983).

10) Y. Yamamoto, R. Kataoka, S. Imahara, and T. Amano, *Bull. Chem. Soc. Jpn.*, **54**, 2972 (1981).

11) Y. Yamamoto, *Chem. Lett.*, **1980**, 1555.

12) Y. Yamamoto and E. Toyota, *Chem. Pharm. Bull.*, **28**, 3153 (1980).

13) J. Endo, *Nippon Kagaku Kaishi.*, **65**, 428 (1944).

14) H. Kuma and S. Yamada, *Bull. Chem. Soc. Jpn.*, **49**,2115 (1976).

15) M. M. Patel and R. P. Patel, *J. Indian Chem. Soc.*, **51**, 770 (1974).

16) S. Yamada, *Coord. Chem. Rev.*, **1**, 415 (1966).

17) S. Yamada, K. Yamanouchi, W. Mori, and M. Kishita, *Bull. Chem. Soc. Jpn.*, **49**, 2111 (1976).

18) K. Yamanouchi and S. Yamada, *Inorg. Chim. Acta.*, **12**, 109 (1975).

19) L. Sacconi, M. Ciampolini, F. Maggio, and F. P. Cavasino, *J. Am. Chem. Soc.*, **84**, 3246 (1962).

20) K. Yamanouchi and S. Yamada, *Bull Chem. Soc. Jpn.*, **49**, 163 (1976).

21) H. Nishikawa and S. Yamada, *Bull. Chem. Soc. Jpn.*, **37**, 1154 (1964).

22) H. Nishikawa, S. Yamada, and R. Tsuchida, *Z. Naturforsch.*, **17b**, 78 (1962).

23) H. Nishikawa, S. Yamada, and R. Tsuchida, *Z. Anorg. Allgem. Chem.*, **316**, 278 (1962).

24) L. Sacconi and M. Ciampolini, *J. Chem. Soc.*, **1964**, 276.

25) B. O. West, *J. Chem. Soc.*, **1962**, 1374.

26) S. Yamada, E. Ohno, and K. Yamanouchi, *Bull. Chem. Soc. Jpn.*, **41**, 535 (1968).

27) S. Yamada and H. Nishikawa, *Bull. Chem. Soc. Jpn.*, **36**, 755 (1963).

28) B. O. West, *J. Chem. Soc.*, **1960**, 4944.

29) A. Chakravorty and R. H. Holm, *Inorg. Chem.*, **3**, 1521 (1964).

30) M. Ciampolini, F. Maggio, and F. P. Cavasino, *Inorg. Chem.*, **3**, 1188 (1964).

31) N. S. Biradar and V. H. Kulkarni, *J. Inorg. Nucl. Chem.*, **33**, 3847 (1971).

32) A. V. D. Bergen, K. S. Murray, and B. O. West, *Aust. J. Chem.*, **25**, 705 (1972).

33) N. S. Biradar and V. H. Kulkarni, *J. Inorg. Nucl. Chem.*, **33**, 2451 (1971).

34) N. S. Biradar and V. H. Kulkarni, *Z. Anorg. Allg. Chem.*, **387**, 275 (1972).

35) Y. Yamamoto and E. Toyota, *Chem. Pharm. Bull.*, **30**, 2262 (1982).

36) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds, "Wiley-Interscience, New York (1970) p.150.

37) J. K. Wilmshurst, *Can. J. Chem.*, **38**, 467 (1960).

38) G. F. Svatos, D. M. Sweeny, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **79**, 3313 (1957).

39) S. Utsuno, A. Hayashi, S. Kondo, and M. Utsumi, *Chem. Lett.*, **1979**, 351.

40) S. Utsuno and M. Sekizaki, *Inorg. Nucl. Chem. Lett.*, **15**, 259 (1979).

41) W. L. Jolly, A. D. Jarris, and T. S. Briggs, *Inorg. Chem.*, **4**, 1064 (1965).

42) L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra, A Collection of Assigned, Coded, and Indexed Spectra," Wiley-Interscience, New York (1972), No. 231, 293.