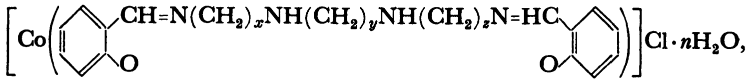
May, 1985] Bull. Chem. Soc. Jpn., 58, 1509—1515 (1985)

Cobalt(III) Complexes with $[\mathrm{N}_{6-n}\mathrm{X}_n]$-type Ligands. V.[1] The Preparation and Properties of *N,N′*-Disalicylidene-substituted Quadridentate Amine Cobalt(III) Complexes

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

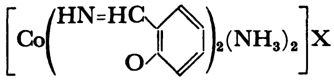
(Received August 4, 1984)

(1,8-*N*-Disalicylidene-3,6-diazaoctane-1,8-diamine)cobalt(III) chloride hydrate (**1a**; *x,y,z*: 2,2,2),



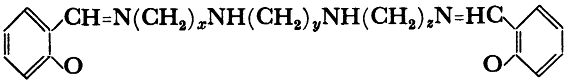
(1,9-*N*-disalicylidene-3,7-diazanonane-1,9-diamine)cobalt(III) chloride (**2a**; *x,y,z*: 2,3,2), (1,10-*N*-disalicylidene-4,7-diazadecane-1,10-diamine)cobalt(III) chloride (**3a**; *x,y,z*: 3,2,3), and (1,11-*N*-disalicylidene-4,8-diazaundecane-1,11-diamine)cobalt(III) chloride hydrate (**4a**; *x,y,z*: 3,3,3) have been isolated from a reaction mixture of $[\mathrm{CoCl_2L}]\mathrm{Cl}\cdot n\mathrm{H_2O}$ (L: quadridentate amine), AgOH, and salicylaldehyde or from one of quadridentate amine, salicylaldehyde, $\mathrm{CoCl_2\cdot 6H_2O}$ and air, and characterized. The ^{1}H and ^{13}C chemical shifts of their amine protons, methylene protons, and methylene carbons have been assigned. The configurations of **1a** and **2a** are the *trans,cis*-(*mf₂m*) configuration for the two CH=N– and two phenoxyl groups of the coordinated *N,N′*-disalicylidene-substituted quadridentate amine ligands. On the other hand, complexes **3a** and **4a** have the *cis,trans*(*fm₂f*) configuration.

Previously, we have been concerned with the preparation and properties of isomers of the mixed ligand complexes of the $[\mathrm{CoN}_{6-n}\mathrm{O}_n]$ type, *e.g.*, the diamminebis(salicylideneaminato)cobalt(III) complexes,[1)]



and salicylato(quadridentate amine)cobalt(III) complexes,[2–5)] $[\mathrm{Co(sal\text{-}R)L]X}\cdot n\mathrm{H_2O}$ (R: H, Me; L: 2,2,2-tet, 2,3,2-tet, 3,2,3-tet, and 3,3,3-tet). Three isomers of the former complexes have been isolated; their configurations are the *trans,trans,trans-*, *trans,cis,cis-*, and *cis,trans,cis*-positions for the two ammine ligands, two CH=NH, and two phenoxyl groups of the coordinated salicylideneaminato ligands respectively. In the latter complexes, the *cis-β₁* and *β₂* isomers have been isolated, and the ^{1}H and ^{13}C chemical shifts of their amine protons,[3)] center methylene, and $\mathrm{NH_2}$– and NH-side methylene protons and carbons[5)] have previously been assigned. The assignments of the =N-side methylene protons and carbons have, however, so far remained unsolved.

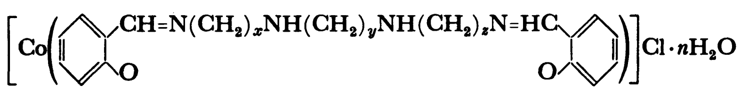
Many investigations of metal complexes (metal: $\mathrm{Cu^{II}}$, $\mathrm{Co^{II}}$, $\mathrm{Ni^{II}}$, $\mathrm{Al^{III}}$, $\mathrm{Ga^{III}}$, $\mathrm{Mn^{III}}$, $\mathrm{Fe^{III}}$, $\mathrm{Co^{III}}$) with the *N,N′*-disalicylidene-substituted quadridentate amine ligand,



(*x,y,z*: 2,2,2), have been reported, especially with regard to their preparation,[6–8)] IR spectra,[6–8)] magnetic susceptibility,[8,9)] and geometrical isomerism,[9)] but the NMR spectra have never been reported. These metal complexes have a *trans,cis*(*mf₂m*)[10,11)] configuration for the two CH=N and two phenoxyl groups, but complexes with a *trans,cis*(*f₄*), *cis,trans*(*fm₂f*) or *cis,cis*-(*f₂mf* or *fmf₂*)[10,11)] configuration have never been described except for iron complexes[12)] with the *N,N′*-disalicylidene-substituted quadridentate amine ligand (*x,y,z*: 3,2,3 and 3,3,3), which has the *cis,-trans*(*fm₂f*) configuration. Even now, the metal complexes with the *N,N′*-disalicylidene-substituted quadridentate amine ligand (*x,y,z*: 2,3,2) have not yet been reported. In addition, very little is known of the properties and general chemistry of the metal complexes with the ligands of *x,y,z*: 2,3,2; 3,2,3 and 3,3,3, in contrast with the large amount of information available on the complexes with the ligand of *x,y,z*: 2,2,2. The present paper deals with the preparation and properties of the cobalt(III) complexes with the *N,N′*-disalicylidene-substituted quadridentate amine ligand (*x,y,z*: 2,2,2; 2,3,2; 3,2,3 and 3,3,3); it also deals with the assignments of the configurations of the isomers and of the ^{1}H and ^{13}C chemical shifts of the =N-side methylene protons and carbons.

Results and Discussion

The (*N,N′*-disalicylidene-substituted quadridentate amine)cobalt(III) chloride hydrates, **1a**, **2a**, **3a**, and **4a** (Scheme 1), have been isolated from a reaction mixture of $[\mathrm{CoCl_2L}]\mathrm{Cl}\cdot n\mathrm{H_2O}$ (L: quadridentate amine),



	x	y	z		x	y	z
1a	2	2	2	**3a**	3	2	3
2a	2	3	2	**4a**	3	3	3

Scheme 1.

AgOH, and salicylaldehyde or from one of quadridentate amine, salicylaldehyde, $CoCl_2\cdot 6H_2O$, and air. The corresponding nitrates (**1b**, **2b**, **3b**, **4b**) and picrates (**1c**, **2c**, **3c**, **4c**) have been prepared from a reaction mixture of silver nitrate or picric acid and **1a**, **2a**, **3a**, or **4a**, respectively.

The electric conductivities of **1a**, **2a**, **3a**, and **4a** in aqueous solutions were 97—103 S cm^2 equiv^{-1}. The IR spectra of these complexes showed a strong peak for CH=N stretching[6,7] at *ca.* 1620 or *ca.* 1640 cm^{-1} and three strong peaks for C–N stretching[6,7] in the 1126—1208 cm^{-1} region. The absorption spectra of **1a** and **3a** are closely similar to those of **2a** and **4a** respectively, as is shown in Fig. 1 and Table 1. The absorption bands at 388—403 nm and at about 590 nm or 628 nm are assigned to the charge-transfer band[13–15] and the first absorption band ($^1T_{1g}\leftarrow{}^1A_{1g}$ in an O_h approximation) respectively.

The ^{1}H NMR spectra of all the complexes were measured in dimethyl sulfoxide (DMSO-d_6) or MeOH-d_4, while the ^{13}C NMR spectra of **1a**, **2a**, **3a**, and **4a** were measured in D_2O. Their spectra suggested a C_2 symmetry, as is shown in Fig. 2. The ^{1}H NMR spectra of **1c** and **3c** are similar to those of **2c** and **4c** respectively. The signals at δ 1.3—4.3 are assigned to the methylene protons of the coordinated *N,N'*-disalicylidene-substituted quadridentate amine ligand (abbreviation: sexidentate ligand). The signals at δ 4.6—6.0 are assigned to the NH protons. The multiplet signals at δ 6.2—7.4 are assigned to the ring protons. The signals at δ 7.6—8.4 are assigned to the CH=N protons. The lowest signals are assigned to the picrate protons. The methylene-proton signals of **1c** and **2c** can be divided into three or four groups at the δ 1.7—2.1, 2.2—2.8, 2.8—3.1, and 4.2—4.3 regions. The signal at δ 1.7—2.1 of **2c** is assigned to the center methylene protons ($NHCH_2C\underline{H}_2CH_2NH$), while the signals at δ 2.2—2.8 and 2.8—3.1 of **1c** and **2c** are assigned to the NH-side methylene protons ($=NCH_2C\underline{H}_2NHC\underline{H}_2-$) of the coordinated sexidentate ligands by comparison with those of salicylato(quadridentate amine)cobalt(III) chloride hydrate, [Co(sal)L]Cl·nH$_2$O (**5**), (L: 2,2,2-tet; 2,3,2-tet; 3,2,3-tet and 3,3,3-tet), previously reported.[5] Thus, the signals at δ 4.2—4.3 of **1c** and **2c** have been assigned to the =N-side methylene protons ($=NC\underline{H}_2CH_2NH$) of the coordinated sexidentate ligands. In the NH-side methylene-proton signals of **2c**, the intensity ratio of two methylene-proton signals at δ 2.35 and 2.86 is 6:2; *i.e.*, the two methylene protons at δ 2.86 are overlapped with those at δ 2.35 because of the influence of C-5 center methylene. Therefore, the signals at δ 2.35 and 2.86 of **2c** can be assigned to the C-3, C-7 methylene protons (*cf.* Table 2) and the C-4, C-6 methylene protons respectively. The signals at δ 2.3—3.6 of **3c** and 1.4—3.9 of **4c** are difficult to assign to the individual methylene protons. The ^{13}C NMR spectra of **1a**, **2a**, **3a**, and **4a** showed 3—5 signals for the quadridentate amine carbons at δ 20—60 and 7 signals at δ 117—170 for the salicylidene carbons, as is shown in Fig. 2. The chemical shifts of the center methylene carbons at δ 20—31, the NH-side methylene carbons at 45—54, and the ring

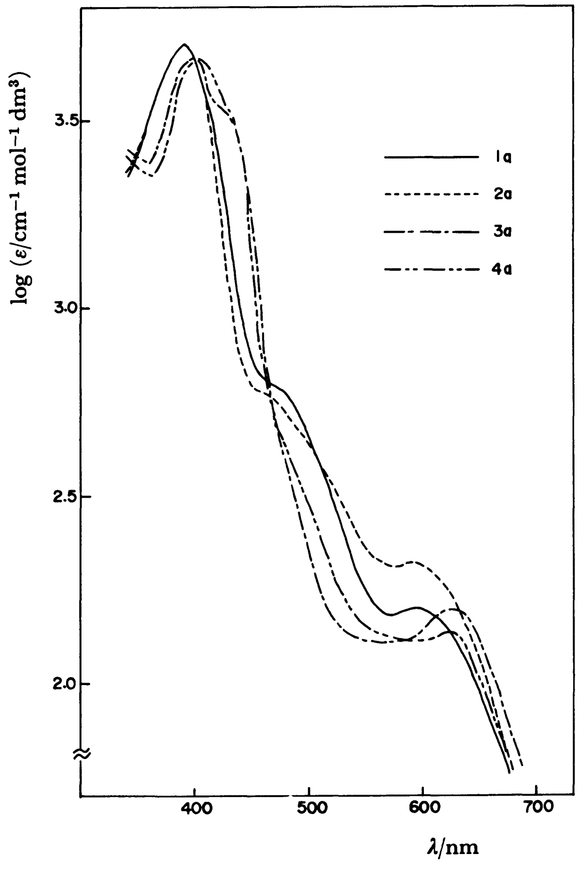


Fig. 1. The electronic absorption spectra of **1a**, **2a**, **3a**, and **4a** complexes in methanol.
1a: [Co(sal$_2$2,2,2-tet)]Cl·H$_2$O, **2a**: [Co(sal$_2$2,3,2-tet)]Cl, **3a**: [Co(sal$_2$3,2,3-tet)]Cl, **4a**: [Co(sal$_2$3,3,3-tet)]Cl·H$_2$O.

Table 1. Some physical properties of complexes

Complex No.	IR spectra cm^{-1} C=N$_{str.}$	C-N$_{str.}$			Absorption bands in methanol λ/nm (ε/cm^{-1} mol^{-1} dm^3)			Decomp θ_m/°C	Electric conductivity of aqueous solutions S cm^2 equiv^{-1}
1a	1642	1204	1150	1129	388(5200)	470 sh(615)	590(155)	236—238	97
1b	1642	1198	1150	1128	388(4900)	470 sh(580)	590(145)	230—233	
1c	1640	1202	1152	1128			590(158)	284—285	
2a	1642	1199	1146	1128	388(5200)	470 sh(566)	590(208)	241—242	103
2b	1644	1200	1149	1129	388(5000)	470 sh(546)	590(200)	236—238	
2c	1644	1198	1148	1128			590(209)	226—228	
3a	1621	1206	1146	1130	398(4610)	430 sh(3270)	628(159)	289—291	103
3b	1620	1206	1144	1128	398(4590)	428 sh(3230)	628(157)	303—305	
3c	1621	1210	1148	1130			628(160)	265—268	
4a	1620	1208	1148	1126	403(4600)	427 sh(3200)	627(135)	256—258	100
4b	1620	1208	1148	1125	403(4550)	427 sh(3160)	628(132)	275—277	
4c	1620	1205	1142	1121			628(136)	236—238	

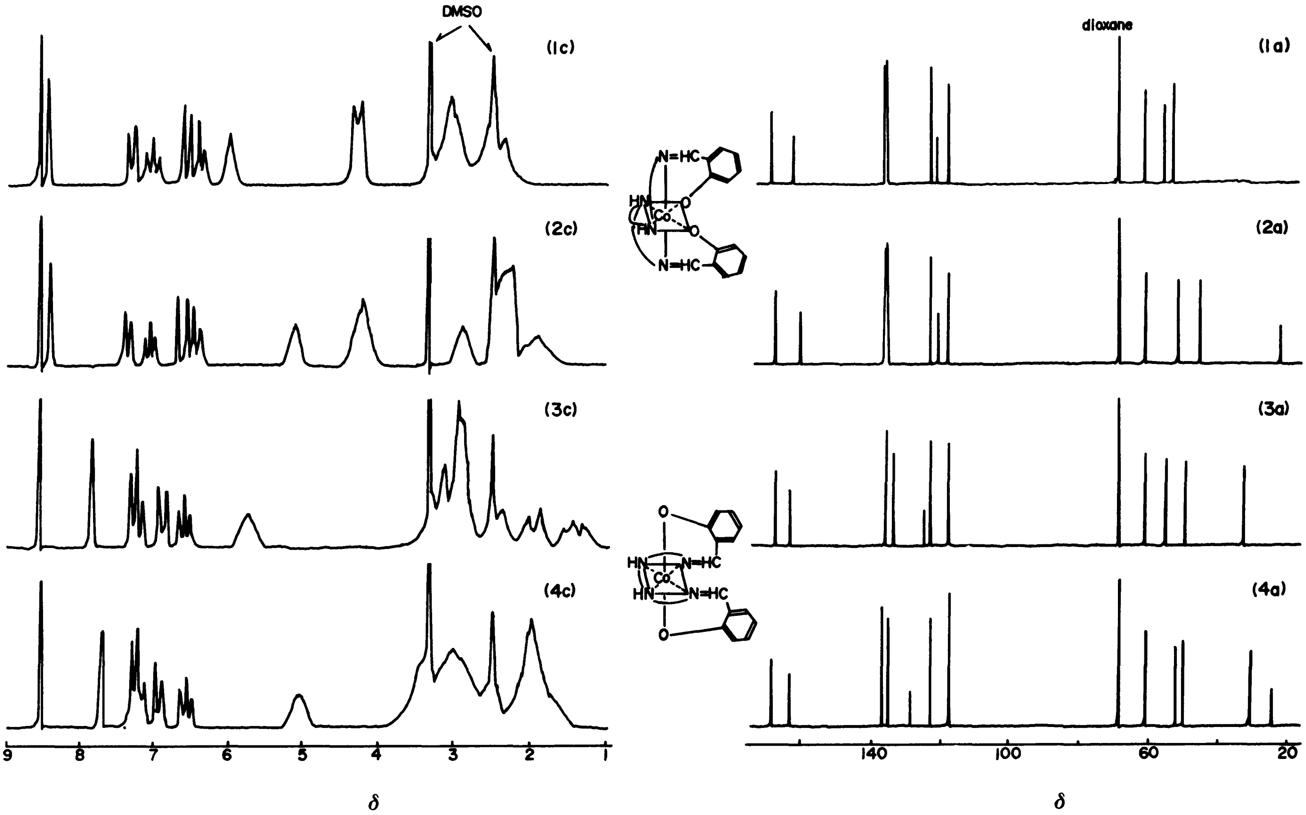
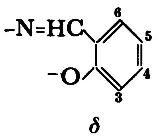
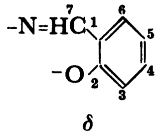


Fig. 2. The ^{1}H and ^{13}C NMR spectra of complexes.
1a: [Co(sal$_2$2,2,2-tet)]Cl·H$_2$O, **1c**: [Co(sal$_2$2,2,2-tet)]pic, **2a**: [Co(sal$_2$2,3,2-tet)]Cl **2c**: [Co(sal$_2$2,3,2-tet)]pic, **3a**: [Co(sal$_2$3,2,3-tet)]Cl, **3c**: [Co(sal$_2$3,2,3-tet)]pic, **4a**: [Co(sal$_2$3,3,3-tet)]Cl·H$_2$O, **4c**: [Co(sal$_2$3,3,3-tet)]pic.

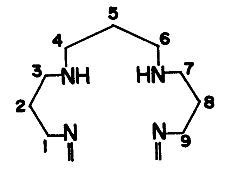
carbons were assigned on the basis of the results of **5**[5] and salicylato(tetraammine)cobalt(III) chloride monohydrate,[16] [Co(sal)(NH$_3$)$_4$]Cl·H$_2$O (**6**), as is shown in Table 2. Thus, the signals at *ca.* δ 60 have been assigned to the =N-side methylene carbons of the coordinated sexidentate ligands. The chemical shifts of the =N-side methylene protons and carbons are lower than those of the NH-side methylene protons and carbons respectively. Therefore, the order of the ^{1}H and ^{13}C chemical shifts of the center, NH$_2$-,[5] NH-, and =N-side methylene protons or carbons is as is shown in Scheme 2;

TABLE 2. ^{1}H AND ^{13}C NMR SPECTRA OF COMPLEXES

^{1}H Complex No.	Methylene protons δ				NH proton δ	 δ					Picrate δ
	Center methylene C-2, C-5, C-8	NH-side methylene C-3, C-7	C-4, C-6	=N-side methylene C-1, C-9		H-5	H-3	H-4	H-6	CH=N	
1a		2.58(4H)	3.07(4H)	4.26(4H)	6.04(2H)	6.28—6.65(m, 4H)		6.97(t, 2H)	7.30(d, 2H)	8.42(2H)$^{1)}$	
1b		2.58(4H)	3.07(4H)	4.25(4H)	5.97(2H)	6.28—6.65(m, 4H)		6.97(t, 2H)	7.28(d, 2H)	8·41(2H)$^{1)}$	
1c		2.2—2.8(4H)	3.15(4H)	4.32(4H)	5.98(2H)	6.30—6.65(m, 4H)		6.99(t, 2H)	7.28(d, 2H)	8.40(2H)	8.52(2H)$^{1)}$
2a	1.87(2H)	2.29(6H)	2.80(2H)	4.20(4H)	5.18(2H)	6.35—6.70(m, 4H)		7.02(t, 2H)	7.35(d, 2H)	8.45(2H)$^{1)}$	
2b	1.90(2H)	2.28(6H)	2.80(2H)	4.20(4H)	5.14(2H)	6.38—6.70(m, 4H)		7.03(t, 2H)	7.35(d, 2H)	8.40(2H)$^{1)}$	
2c	1.7—2.1(2H)	2.35(6H)	2.86(2H)	4.22(4H)	5.18(2H)	6.35—6.70(m, 4H)		7.03(t, 2H)	7.32(d, 2H)	8.40(2H)	8.52(2H)$^{1)}$
3a	1.3—2.1(4H)	2.4—3.8(12H)$^{a)}$			5.30(2H)	6.56(t, 2H)	6.90(d, 2H)	7.02—7.30(m, 4H)		7.65(2H)$^{2)}$	
3b	1.2—2.1(4H)	2.3—3.7(12H)$^{a)}$			5.72(2H)	6·55(t, 2H)	6.85(d, 2H)	7.05—7.33(m, 4H)		7.80(2H)$^{1)}$	
3c	1.2—2.2(4H)	2.3—3.6(12H)$^{a)}$			5.75(2H)	6.54(t, 2H)	6.84(d, 2H)	7.05—7.32(m, 4H)		7.80(2H)	8.50(2H)$^{1)}$
4a		1.4—3.9(18H)$^{b)}$			4.60$^{c)}$	6.65(t, 2H)	6.95(d, 2H)	7.05—7.30(m, 4H)		7.57(2H)$^{2)}$	
4b		1.5—3.9(18H)$^{b)}$			5.02(2H)	6.55(t, 2H)	6.91(d, 2H)	7.07—7.31(m, 4H)		7.68(2H)$^{1)}$	
4c		1.4—3.9(18H)$^{b)}$			5.00(2H)	6.53(t, 2H)	6.90(d, 2H)	7.05—7.34(m, 4H)		7.70(2H)	8.50(2H)$^{1)}$

^{13}C	Center methylene carbon δ		NH-side methylene carbon δ		=N-side methylene carbon δ	 δ						
	C-5	C-2 C-8	C-3, C-4 C-6 and C-7		C-1 C-9	C-1	C-2	C-3	C-4	C-5	C-6	C-7
1a			51.9	54.2	59.5	120.5	163.2	117.3	136.2	122.3	136.0	169.5$^{3)}$
2a	20.5		45.4	50.5	60.0	120.7	162.2	117.7	136.4	122.9	136.0	168.7$^{3)}$
3a		31.1	49.0	53.7	59.7	125.1	164.3	117.7	136.1	123.5	134.4	169.0$^{3)}$
4a	23.3	28.8	49.2	50.7	59.8	129.0	165.4	117.3	136.4	123.0	135.0	169.6$^{3)}$

Solvents and Standard: 1) DMSO-d_6, internal TMS; 2) MeOH-d_4, internal TMS; 3) D_2O, internal dioxane ($\delta=0$). a) This signal contains the NH-side and =N-side methylene proton signals. b) This signal contains the center methylene, NH-side methylene, and =N-side methylene proton signals. c) This signal overlaps with the signal of the solvent.



Positions of the methylene protons or carbon in complexes.

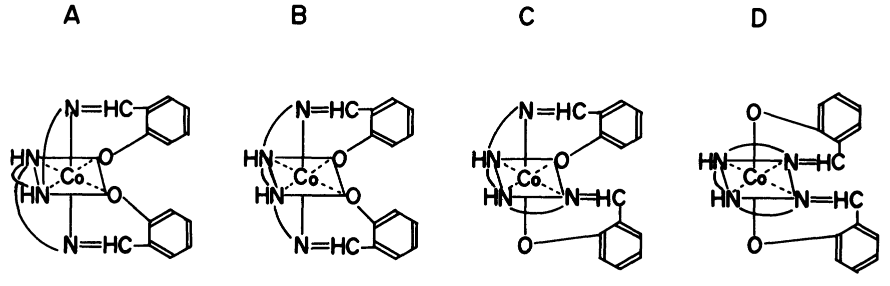
$=\mathrm{N\underline{CH}_2(CH_2)_{\mathit{n}}CH_2NH}<\mathrm{NH_{\mathit{m}}CH_2(CH_2)_{\mathit{n}}\underline{CH}_2NH}<\mathrm{NH_2\underline{CH}_2CH_2NH}<\mathrm{NH_2\underline{CH}_2CH_2CH_2NH}$

=N-side methylene protons (or carbon) NH-side methylene protons (or carbon) $\mathrm{NH_2}$-side methylene protons (or carbon)

$<=\mathrm{NCH_2\underline{CH}_2CH_2NH}<\mathrm{NHCH_2\underline{CH}_2CH_2NH}<\mathrm{NH_2CH_2\underline{CH}_2CH_2NH}$ $\left(\begin{array}{l} m:\ 0,\ 1 \text{ or } 2 \\ n:\ 0 \text{ or } 1 \end{array}\right)$

center methylene protons (or carbon)

Scheme 2.



trans,cis ($\mathrm{mf_2m}$) trans,cis ($\mathrm{f_4}$) cis,cis ($\mathrm{f_2mf}$ or $\mathrm{fmf_2}$) cis,trans ($\mathrm{fm_2f}$)

Fig. 3. The configurations of (*N,N'*-disalicylidene-substituted quadridentate amine)cobalt(III) complexes.

Complexes **1a**, **2a**, **3a**, and **4a** have four isomers of **A**, **B**, **C**, and **D**, as is shown in Fig. 3. The configurations of **A**, **B**, and **D** have a C_2 symmetry, while the configuration of **C** has a C_1 symmetry. The IR, ^{1}H, and ^{13}C NMR spectra of Complexes **1a**, **2a**, **3a**, and **4a** are suggestive of a C_2 symmetry;[13,15,17,18] *i.e.*, the isomers of these complexes can be assigned to the **A**, **B**, or **D** configurations. A clear distinction between one group of **1a**, **2a** complexes and the other group of **3a**, **4a** complexes was found in the color, solubility, IR, electronic absorption, NMR spectra, and the Dreiding stereo model. **1a** and **2a** are brown, while **3a** and **4a** are green. Complexes **1a** and **2a** are very soluble in DMSO, though **3a** and **4a** are only slightly soluble. The C=N stretching signals (at 1642 cm^{-1} for **1a** and at 1620 cm^{-1} for **3a**) in the IR spectra, the electronic absorption bands (at 388, 470, and 590 nm for **1a** and at 398, 430, and 628 nm for **3a**), and the methylene-proton signals, the CH=N proton signals (at δ 8.4 for **1a** and at δ 7.6 for **3a**), and the ring-proton signals (multiplet, triplet, and doublet signals for **1a** and triplet, doublet, and multiplet signals for **3a**) of the ^{1}H NMR spectra of **1a** and **3a** are closely similar to those of **2a** and **4a** respectively, as is shown in Tables 1 and 2. In the Dreiding stereo model, the methylene-loop rings of the coordinated sexidentate ligands of former complexes show that the **A** isomer[6] is not strained, though the other isomers, **B** and **D**, are greatly strained. Thus, the complexes of the former group are assigned to the **A** isomer, which has a *trans,cis*(*mf*$_2$*m*)[10,11] configuration[6] for the two CH=N and two phenoxyl groups. On the other hand, in the methylene-loop rings of the latter complexes, the **A**, **B**, and **D** isomers are not strained, though the methylene protons of the methylene-loop ring of the **A** and **B** isomers have a steric repulsion because of the non-planar structure. It has been established that, in iron[8,9,12] and cobalt[19] complexes of $[\mathrm{Fe^{III}Sal_2}3,2,3\text{-tet}]^+$, and $[\mathrm{Fe^{III}Sal_2}2,2,2\text{-tet}]^+$ and of $[\mathrm{Co^{III}Cl_2}3,2,3\text{-tet}]^+$, $[\mathrm{Co^{III}Cl_2}2,2,2\text{-tet}]^+$, the 3,2,3-tet ligand takes a structure with four nitrogens in plane, while the 2,2,2-tet ligand usually adopts a non-planar structure. Thus, the complexes of the latter group are assigned to the **D** isomer, which has a *cis,trans* (*fm*$_2$*f*)[10,11] configuration for the two CH=N and two phenoxyl groups. The color, solubility, IR, electronic absorption, and NMR spectra of the latter complexes are very different from those of the former complexes. These differences are due to the configuration of the complexes.

Experimental

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

*Preparation of Complexes. (1,8-*N*-Disalicylidene-3,6-diazaoctane-1,8-diamine)cobalt(III) Chloride (**1a**): Method A: cis-α* or *β*-Dichloro(3,6-diazaoctane-1,8-diamine(trien))cobalt(III) chloride[20,21] (3.0 g, 9.63 mmol) was added to moistened fresh AgOH, which has been made from silver nitrate (3.27 g, 19.25 mmol) and potassium hydroxide (1.08 g, 19.25

mmol). The mixture was stirred for several minutes at room temperature and then stirred for about 40 min at 60 °C. The silver chloride thus precipitated was filtered off. A methanol solution (20 cm^3) of salicylaldehyde (2.36 g, 19.33 mmol) was then added, drop by drop, to the reddish violet filtrate. The solution was stirred at 50 °C for 24 h. The solution was concentrated on a rotary evaporator, and the reaction mixture was dried over silica gel. Complex **1a** was extracted with dry methanol or dry ethanol from the dried reaction mixture. The purification of the complexes was achieved by column chromatography on alumina. When the solvent was then eluted with methanol or ethanol, the effluent of the first brown band of Complex **1a** was collected and the solution was concentrated. Then, the precipitated complex was recrystallized twice from ethanol–ether (3:2). Yield: 2.41 g (53.8%).

No other isomer was isolated from the second red band and third pink bands, which perhaps $[CoCl(OH)trien]^+$ or $[Co(OH)_2trien]^+$.[22]

Method B: A methanol solution (10 cm^3) of trien (1.46 g, 9.98 mmol) was added to a methanol solution (40 cm^3) of salicylaldehyde (2.44 g, 19.98 mmol), and the mixture was stirred 10 min at room temperature. Then, the solution was added to a methanol solution (50 cm^3) of $CoCl_2 \cdot 6H_2O$ (2.38 g, 10.0 mmol). Air was bubbled into the solution for 7 h, and the solution was concentrated on a rotary evaporator. The complex thus precipitated was recrystallized twice from water–acetone or ethanol–ether. Yield: 2.34 g (50.4%). Found: C, 51.41; H, 6.00; N, 12.04; Cl, 8.02%. Calcd for $CoC_{20}H_{26}N_4O_3Cl$ (MW 464.84) C, 51.68; H, 5.64; N, 12.05; Cl, 7.63%. Color: brownish black.

*(1,8-*N*-Disalicylidene-3,6-diazaoctane-1,8-diamine)cobalt(III) Nitrate Hydrate (**1b**)*: An aqueous solution of silver nitrate (0.18 g, 1.06 mmol) was added to an aqueous solution of **1a** (0.48 g, 1.03 mmol). The mixture was stirred, and the silver chloride thus precipitated was filtered. The filtrate was concentrated on a rotary evaporator. Then, the precipitated complex was recrystallized twice from methanol–ether. Yield: 0.22 g (43.4%). Found: C, 48.56; H, 5.69; N, 14.22%. Calcd for $CoC_{20}H_{26}N_5O_6$ (MW 491.39) C, 48.89; H, 5.33; N, 14.25%. Color: brown.

*(1,8-*N*-Disalicylidene-3,6-diazaoctane-1,8-diamine)cobalt(III) Picrate (**1c**)*: An aqueous solution of picric acid (0.10 g, 0.436 mmol) was added to an aqueous solution of **1a** (0.20 g, 0.430 mmol). The mixture was stirred, and then the precipitated complex was filtered, washed with water, and dried. Yield: 0.26 g (94.5%). Found: C, 48.80; H, 4.28; N, 15.89%. Calcd for $CoC_{26}H_{26}N_7O_9$ (MW 639.47) C, 48.84; H, 4.10; N, 15.33%. Color: yellowish brown.

*(1,9-*N*-Disalicylidene-3,7-diazanonane-1,9-diamine)cobalt(III) Chloride (**2a**)*: A methanol solution (10 cm^3) of 3,7-diazanonane-1,9-diamine (2,3,2-tet) (1.60 g, 9.98 mmol) was added to a methanol solution (40 cm^3) of salicylaldehyde (2.44 g, 19.98 mmol), after which the mixture was stirred 10 min at room temperature. Then the solution was added to a methanol solution (50 cm^3) of $CoCl_2 \cdot 6H_2O$ (2.38 g, 10.0 mmol). Air was bubbled into the solution for 7 h, the solution was concentrated in a rotary evaporator, and the reaction mixture was dried over silica gel. Complex **2a** was extracted with dry methanol from the dried mixture. The purification of the complexes was achieved by column chromatography on alumina. When the solvent was eluted with methanol, the effluent of the first brown band of Complex **2a** was collected and the solution was concentrated. Then, the precipitated complex was recrystallized twice from methanol–acetone–ether. Yield: 1.20 g (26.1%). Found: C, 54.51; H, 6.01; N, 12.07; Cl, 7.93%. Calcd for $CoC_{21}H_{26}N_4O_2Cl$ (MW 460.85) C, 54.73; H, 5.69; N, 12.16; Cl, 7.69%. Color: brownish black.

*(1,9-*N*-Disalicylidene-3,7-diazanonane-1,9-diamine)cobalt(III) Nitrate (**2b**)*: Complex **2b** has been prepared from the reaction mixture of silver nitrate (0.18 g, 1.06 mmol) and Complex **2a** (0.46 g, 0.998 mmol) according to the method used for **1b**. Yield: 0.16 g (32.9%). Found: C, 51.11; H, 5.08; N, 14.60%. Calcd for $CoC_{21}H_{26}N_5O_5$ (MW 487.40) C, 51.75; H, 5.38; N, 14.37%. Color: brown.

*(1,9-*N*-Disalicylidene-3,7-diazanonane-1,9-diamine)cobalt(III) Picrate (**2c**)*: Complex **2c** has been prepared from the reaction mixture of **2a** (0.2 g, 0.434 mmol) and picric acid (0.1 g, 0.436 mmol) according to the method used for **1c**. Yield: 0.16 g (56.4%). Found: C, 49.28; H, 4.49; N, 15.04%. Calcd for $CoC_{27}H_{28}N_7O_9$ (MW 653.49) C, 49.62; H, 4.32; N, 15.00%. Color: yellowish brown.

*(1,10-*N*-Disalicylidene-4,7-diazadecane-1,10-diamine)cobalt(III) Chloride (**3a**)*: Complex **3a** has been prepared from a reaction mixture of *trans*-dichloro(4,7-diazadecane-1,10-diamine)cobalt(III) chloride hydrate[23] (3.0 g, 8.39 mmol), AgOH (2.09 g, 16.74 mmol) which had been obtained from silver nitrate, and potassium hydroxide and salicylaldehyde (2.05 g, 16.79 mmol) according to the method used for **A** of **1a**. The green complex of **3a** was recrystallized twice from methanol–ether. Yield: 0.75 g (18.8%). Found: C, 55.49; H, 5.72; N, 12.09; Cl, 8.02%. Calcd for $CoC_{22}H_{28}N_4O_2Cl$ (MW 474.88) C, 55.64; H, 5.94; N, 11.80; Cl, 7.47%. Color: green.

*(1,10-*N*-Disalicylidene-4,7-diazadecane-1,10-diamine)cobalt(III) Nitrate (**3b**)*: Complex **3b** was prepared from the reaction mixture of Complex **3a** (0.47 g, 0.99 mmol) and silver nitrate (0.17 g, 1.00 mmol) according to the method used for **1b**. Yield: 0.22 g (44.3%). Found: C, 52.70; H, 5.78; N, 14.01%. Calcd for $CoC_{22}H_{28}N_5O_5$ (MW 501.43) C, 52.70; H, 5.63; N, 13.97%. Color: green.

*(1,10-*N*-Disalicylidene-4,7-diazadecane-1,10-diamine)cobalt(III) Picrate (**3c**)*: This complex was prepared from the reaction mixture of Complex **3a** (0.16 g, 0.337 mmol) and picric acid (0.08 g, 0.349 mmol) according to the method used for **1c**. Yield: 0.18 g (80.0%). Found: C, 50.64; H, 4.51; N, 15.09%. Calcd for $CoC_{28}H_{30}N_7O_9$ (MW 667.52) C, 50.38; H, 4.53; N, 14.69%. Color: yellowish green.

*(1,11-*N*-Disalicylidene-4,8-diazaundecane-1,11-diamine)cobalt(III) Chloride Hydrate (**4a**)*: A methanol solution (10 cm^3) of 4,8-diazaundecane-1,11-diamine (3,3,3-tet) (1.88 g, 9.98 mmol) was added to a methanol solution (40 cm^3) of salicylaldehyde (2.44 g, 19.98 mmol), and the mixture was stirred 10 min at room temperature. Then, the solution was added to a methanol solution (50 cm^3) of $CoCl_2 \cdot 6H_2O$ (2.38 g, 10.0 mmol). Air was bubbled into the solution for 7 h, and the solution was concentrated on a rotary evaporator. The concentrated solution was submitted to a column chromatography on alumina. On eluting the solvent with methanol, the eluent of the first brown band was collected and concentrated. The purification of the complex was achieved by the use of a column of ion-exchange resin (SP-Sephadex C-25 Na^+ form). After the mixture had been

eluted with 0.2 mol dm^{-3} of NaCl the fourth green band of Complex **4a** was collected and concentrated on a rotary evaporator, and the precipitated NaCl was removed by filtration. The green complex was recrystallized twice from methanol-ether. Yield: 0.43 g (8.5%). Found: C, 54.92; H, 6.55; N, 10.72; Cl, 7.31%. Calcd for $CoC_{23}H_{32}N_4O_3Cl$ (MW 506.92) C, 54.50; H, 6.36; N, 11.05; Cl, 6.99%. Color: green.

Attempts to isolate another isomer from this reaction mixture were unsuccessful, because the other bands in the column of the ion-exchange resin were small.

(1,11-N-Disalicylidene-4,8-diazaundecane-1,11-diamine)cobalt(III) Nitrate (4b): This complex was prepared from the reaction mixture of Complex **4a** (0.50 g, 0.986 mmol) and silver nitrate (0.17 g, 1.00 mmol) according to the method used for **1b**. Yield: 0.26 g (51.1%). Found: C, 53.51; H, 5.59; N, 13.28%. Calcd for $CoC_{23}H_{30}N_5O_5$ (MW 515.45) C, 53.59; H, 5.87; N, 13.59%. Color: green.

(1,11-N-Disalicylidene-4,8-diazaundecane-1,11-diamine)cobalt(III) Picrate (4c): This complex was prepared from the reaction mixture of Complex **4a** (0.19 g, 0.375 mmol) and picric acid (0.09 g, 0.393 mmol) according to the method used for **1c**. Yield: 0.23 g (90.0%). Found: C, 51.29; H, 5.04; N, 14.24%. Calcd for $CoC_{29}H_{32}N_7O_9$ (MW 681.55) C, 51.11; H, 4.73; N, 14.39%. Color: yellowish green.

Solubility: Complexes **1a**—**c** and **2a**—**c** are very soluble in DMSO, DMF, and methanol and are soluble in ethanol. Complexes **1a**—**b** and **2a**—**b** are very soluble in water, though **1c** and **2c** are insoluble in water. Complexes **3a** and **4a** are soluble in methanol, though they are only slightly soluble in water, DMSO, and DMF. Complexes **3b**—**c** and **4b**—**c** are soluble in DMSO, DMF and methanol, though they are insoluble in water.

References

1) Part IV. Y. Yamamoto and E. Toyota, *Bull. Chem. Soc. Jpn.*, **57**, 2650 (1984).

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

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

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

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

6) B. D. Sarma and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **77**, 5476 (1955).

7) B. D. Sarma, K. R. Ray, R. E. Sievers, and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **86**, 14 (1964).

8) M. F. Tweedle and L. J. Wilson, *J. Am. Chem. Soc.*, **98**, 4824 (1976).

9) E. Sinn, G. Sim, E. V. Dose, M. F. Tweedle, and L. J. Wilson, *J. Am. Chem. Soc.*, **100**, 3375 (1978).

10) Y. Yoshikawa, *Bull. Chem. Soc. Jpn.*, **49**, 159 (1976).

11) IUPAC Nomenclature of Inorganic Chemistry, Definitive Rules 1970, Butterworths, London (1971).

12) T. Ito, M. Sugimoto. H. Ito, K. Toriumi, H. Nakayama, W. Mori, and M. Sekizaki, *Chem. Lett.*, **1983**, 121.

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

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

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

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

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

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

19) M. D. Alexander and H. G. Hamilton, Jr., *Inorg. Chem.*, **8**, 2131 (1969).

20) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **6**, 787 (1967).

21) "Shin Jikken Kagaku Koza," ed by the Chemical Society of Japan, Maruzen, Tokyo (1977), Vol. 8, Chap. 3, p. 1445.

22) E. Kyuno, L. J. Boucher, and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **87**, 4458 (1965).

23) B. Bosnich, J. M. Harrowfield, and H. Boucher, *Inorg. Chem.*, **14**, 815 (1975).