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Cobalt(III) Complexes with Quadridentate Ligands. III.[1) The Preparation and Properties of the Salicylato or Dichloro(quadridentate amine)cobalt(III) Complexes

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In the ^{1}H and ^{13}C NMR spectra of *trans-* or *cis*-dichloro(quadridentate amine)cobalt(III) chloride hydrates, $[CoCl_2L]Cl\cdot nH_2O$ (L: 2,2,2-tet(trien) (**1a**), 2,3,2-tet (**1b**), 3,2,3-tet (**1c**), and 3,3,3-tet (**1d**)), the signals of their methylene protons and methylene carbons have been assigned to the individual methylene protons and methylene carbon of the coordinated quadridentate amine ligands. The order of ^{1}H and ^{13}C chemical shift of their methylene protons and methylene carbon is as follows:

$$NH_2CH_2(CH_2)_n\underline{CH}_2NH\underline{CH}_2\text{–}<NH_2\underline{CH}_2(CH_2)_nCH_2NH<NH_mCH_2\underline{CH}_2CH_2NH \quad \begin{pmatrix} m\text{: 1 or 2} \\ n\text{: 0 or 1} \end{pmatrix}$$

NH-side methylene protons (or carbon) NH$_2$-side methylene protons (or carbon) Center methylene protons (or carbon)

Thus, the signal of the center methylene protons (or carbon) of the coordinated quadridentate amine ligands appears at higher field than that of the NH-side methylene protons (or carbon). *cis*-β_1-Salicylato(3,7-diazanonane-1,9-diamine)cobalt(III) chloride hydrate, *cis*-β_1-$[Co(sal)(2,3,2\text{-tet})]Cl\cdot H_2O$ (**3b**), and *cis*-β_2-salicylato(quadridentate amine)cobalt(III) chloride hydrates, *cis*-β_2-$[Co(sal)L]Cl\cdot nH_2O$ (L: 2,3,2-tet (**4b**), 3,2,3-tet (**4c**) and 3,3,3-tet (**4d**)) have been isolated from a reaction mixture of sodium salicylate or salicylic acid and **1b**—**d**. The properties of **3b** and **4b** are similar to those of the previously reported complexes **3a** (L: 2,2,2-tet, β_1-form) and **4a** (L: 2,2,2-tet, β_2-form), respectively. Those of **4c** are similar to those of **4d**. Complex **4d** is the most unstable complex among **4a**—**d**. This property is attributable to the center methylenes of the coordinated quadridentate amine ligands.

Many investigations of metal complexes with quadridentate amine ligands, *e.g.*, with 2,2,2-tet(trien), 2,3,2-tet, and 3,3,3-tet, have been reported especially in the field of stereochemistry[2–7)] and NMR spectra.[7–13)] In the NMR spectra, the investigations of methylene protons and methylene carbons of the coordinated quadridentate amine ligands in complexes have received little attention. This is probably because the methylene proton and methylene carbon signals of the coordinated quadridentate amine ligands are close together, and they have not previously assigned separately.

Previous paper[11)] has been concerned with the preparation and properties of the *cis*-β_1 and *cis*-β_2-$[Co(sal)(2,2,2\text{-tet})]Cl\cdot H_2O$. The present paper deals with the assignments of the methylene protons and methylene carbons of the coordinated quadridentate amine ligands of *trans-* or *cis*-$[CoCl_2L]Cl\cdot nH_2O$ (L: 2,2,2-tet, 2,3,2-tet, 3,2,3-tet, and 3,3,3-tet) on their NMR spectra, and deals with the preparation and properties of the *cis*-β_1-$[Co(sal)(2,3,2\text{-tet})]Cl\cdot H_2O$, and *cis*-$\beta_2$-$[Co(sal)L]Cl\cdot nH_2O$ (L: 2,3,2-tet, 3,2,3-tet, and 3,3,3-tet).

Results and Discussion

cis-α-Dichloro(3,6-diazaoctane-1,8-diamine)cobalt(III) Chloride, $[CoCl_2(2,2,2\text{-tet})]Cl$ *(**1a**) and trans-Dichloro(quadridentate amine)cobalt(III) Chloride Hydrates,* $[CoCl_2L]Cl\cdot nH_2O$ *L: 2,3,2-tet, n=2.5 (**1b**); L: 3,2,3-tet, n=1 (**1c**); and L: 3,3,3-tet, n=1 (**1d**)*: The ^{1}H NMR spectra of **1a**—**d** were measured in 0.01 and 1.8 mol dm^{-3} D_2SO_4. The methylene proton signals of the coordinated quadridentate amine ligands in **1a**—**d** can be divided into three groups at 1.5—2.4, 2.3—3.0, and 2.8—3.8 ppm as shown in Fig. 1 and Table 1. The signals (1.5—2.4 ppm) at highest field of **1b**—**d** can be assigned to the center methylene protons ($NHCH_2C\underline{H}_2CH_2NH_{1\text{ or }2}$) of the ligands, because the total number of the center methylene protons of **1b**, **1c**, and **1d** is 2, 4, and 6, respectively. The signals at 2.3—3.0 ppm (4H) of **1a**, **1b**, and **1d** can be assigned to the NH$_2$-side methylene protons ($NHCH_2(CH_2)_nC\underline{H}_2NH_2$ *n*: 0 or 1), and the signals (2.8—3.8 ppm, 8H) at a low field of **1a**, **1b** and **1d** are assigned to the NH-side methylene protons ($\text{–}C\underline{H}_2NHC\underline{H}_2(CH_2)_nCH_2NH_2$ *n*: 0 or 1) of the quadridentate ligands. The difference of chemical shifts of the NH$_2$ and NH-side methylene protons can be attributed to the properties of the terminal NH$_2$ and secondary NH. Thus, the order of the ^{1}H chemical shifts is given as Scheme 1.

$$NH_2CH_2(CH_2)_nC\underline{H}_2NHC\underline{H}_2\text{–}<NH_2C\underline{H}_2(CH_2)_nCH_2NH$$

NH-side methylene protons NH$_2$-side methylene protons

$$<NH_mCH_2C\underline{H}_2CH_2NH \quad \begin{pmatrix} m\text{: 1 or 2} \\ n\text{: 0 or 1} \end{pmatrix}$$

Center methylene protons

Scheme 1.

The ^{1}H NMR spectra of the *trans*-dichloro(2,2,2-tet)-cobalt(III) chloride hydrate hydrochloric acid, *trans*-$[CoCl_2(2,2,2\text{-tet})]Cl\cdot H_2O\cdot HCl$ (**2a**), could not be measured in DMSO-d_6, CF_3COOH, 0.01, 0.1 and 1.8 mol dm^{-3} D_2SO_4, because of isomerization to the *cis*-form. The chemical shifts of the terminal NH$_2$ protons and secondary NH protons of **1a**—**d** are collected in Table 1.

The ^{13}C NMR spectra of **1b**—**d** were measured in D_2O. Both the signal at 28.8 ppm of **1b** and that at 23.5 ppm of **1d** can be assigned to the center methylene carbon (C-5) of the quadridentate ligands as shown in

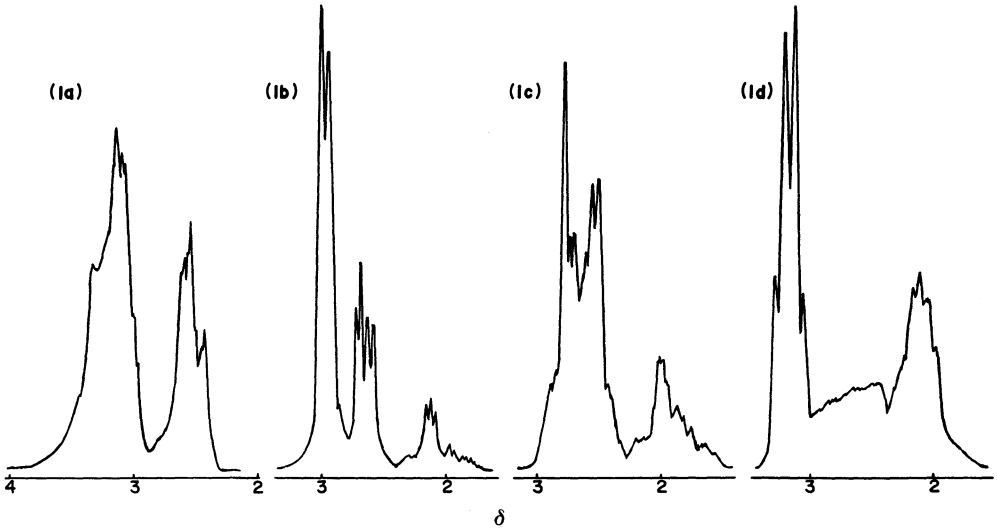


Fig. 1. The ^1H NMR spectra of **1a**—**d** complexes. (**1a**): *cis-α*-$[CoCl_2(2,2,2\text{-tet})]Cl$ in 0.01 mol dm^{-3} D_2SO_4. (**1b**): *trans*-$[CoCl_2(2,3,2\text{-tet})]Cl \cdot 2.5H_2O$ in 0.01 mol dm^{-3} D_2SO_4. (**1c**): *trans*-$[CoCl_2(3,2,3\text{-tet})]Cl \cdot H_2O$ in 0.01 mol dm^{-3} D_2SO_4. (**1d**): *trans*-$[CoCl_2(3,3,3\text{-tet})]Cl \cdot H_2O$ in 1.8 mol dm^{-3} D_2SO_4.

TABLE 1. ^1H NMR SPECTRA OF COMPLEXES **1a**—**d**, **3a**, **3b**, AND **4a**—**d**

Complex No.	Center methylene protons $NHCH_2C\underline{H}_2CH_2NH_2$ $NHCH_2C\underline{H}_2CH_2NH$ δ	NH_2-side methylene protons $NHCH_2C\underline{H}_2NH_2$ $NHCH_2CH_2C\underline{H}_2NH_2$ δ	NH-side methylene protons $-C\underline{H}_2NHC\underline{H}_2CH_2NH_2$ $-C\underline{H}_2NHC\underline{H}_2CH_2CH_2NH_2$ δ	$[NH_2]$ $N(1)H_2$ δ	[NH] $N(4)H_2$ δ	N(3)H δ	[N(2)H+Salicylato] N(2)H δ	[N(2)H+Salicylato] Salicylato δ	Solvents
1a	—	2.3—2.9(4H)	2.9—3.8(8H)	[5.6(4H)]	[6.1(2H)]				1
1b	1.7—2.4(2H)	2.4—2.8(4H)	2.8—3.3(8H)	[5.3(4H)]	[6.0(2H)]				1
1c	1.5—2.3(4H)	2.3—3.0(12H)		[4.9(4H)]	[5.9(2H)]				1
1d	1.7—2.4(6H)	2.4—3.0(4H)	3.0—3.4(8H)	[4.7(4H)]	[5.1(2H)]				2
3a$^{a)}$	—	2.39—3.76(12H)		4.34(1H)4.57(1H)	4.81(1H)5.23(1H)	6.20(1H)	6.51(1H)	6.66—8.00(4H)	2
3b	1.68—2.29(2H)	2.29—3.30(12H)		4.12(2H)	5.13(3H)		6.25(1H)	6.51—7.89(4H)	2
4a$^{a)}$	—	2.38—2.80(3H)	2.80—3.80(9H)	4.34(2H)	4.76(1H)5.21(1H)	6.07(1H)	[6.49—7.97(5H)]		2
4b	1.71—2.01(2H)	2.01—2.45(3H)	2.45—3.18(9H)	4.35(2H)	4.86(2H)	5.20(1H)	6.32(1H)	6.55—7.85(4H)	2
4c	1.44—1.97(4H)	1.97—2.40(3H)	2.40—3.20(9H)	3.32(1H)4.14(1H)	4.71(2H)	5.12(1H)	6.31(1H)	6.57—7.92(4H)	2
4d	1.48—2.24(9H)		2.24—3.23(9H)	3.54—3.97(1H)	3.97—4.93(4H)		5.21(1H)	6.57—7.91(4H)	2

Solvents: 1) 0.01 mol dm^{-1} D_2SO_4; 2) 1.8 mol dm^{-3} D_2SO_4.
Standard: internal DSS. a) Ref. 11.

TABLE 2. ^{13}C NMR SPECTRA OF COMPLEXES **1b**—**d** AND **4a**—**d**

Complex No.	Center methylene carbon δ		NH_2-side methylene carbon δ	NH-side methylene carbon δ	
	C-5	C-2 and C-8	C-1 and C-9	C-3 and C-7,	C-4 and C-6
1b	28.8	—	43.3	55.6	49.1
1c	—	27.7	39.8	49.4	53.3
1d	23.5	24.6	37.5	45.6	45.6
4a	—	—	[42.0, 47.5]	[48.3, 49.7,	52.1, 52.7]
4b	23.6	—	43.1	[51.0, 55.3]	[45.7, 47.2]
4c	—	[21.9, 27.2]	[37.0, 38.5]	[45.2, 47.6]	[48.3, 52.9]
4d	22.9	[24.5, 26.3]	[37.8, 38.8]	[47.3, 49.5,	50.4, 52.8]

Solvent: D_2O, internal dioxane (δ=67.4 ppm). [ ]: The chemical shifts could not be assigned to the individual methylene carbon.

Fig. 2. The signals at 27.7 ppm of **1c** and at 24.6 ppm of **1d** can be assigned to the center methylene carbons (C-2 and C-8) of the ligands. In the **1d** complex, the intensity ratio of the two signals at 37.5 and 45.6 ppm is 1 : 2. The signal at 37.5 ppm can be assigned to the NH_2-side methylene carbons (C-1 and C-9) of the coordinated 3,3,3-tet ligand, and the signal at 45.6 ppm can be assigned to the NH-side methylene carbons (C-3, C-4, C-6, and C-7) of that ligand. Thus, the signal of the NH_2-side methylene carbons of the quadridentate ligands is observed at higher field than that of the NH-side methylene carbons. The signal at 49.1 ppm of **1b** may be assigned to C-4 and C-6 methylene carbons (neighboring methylene carbons of center

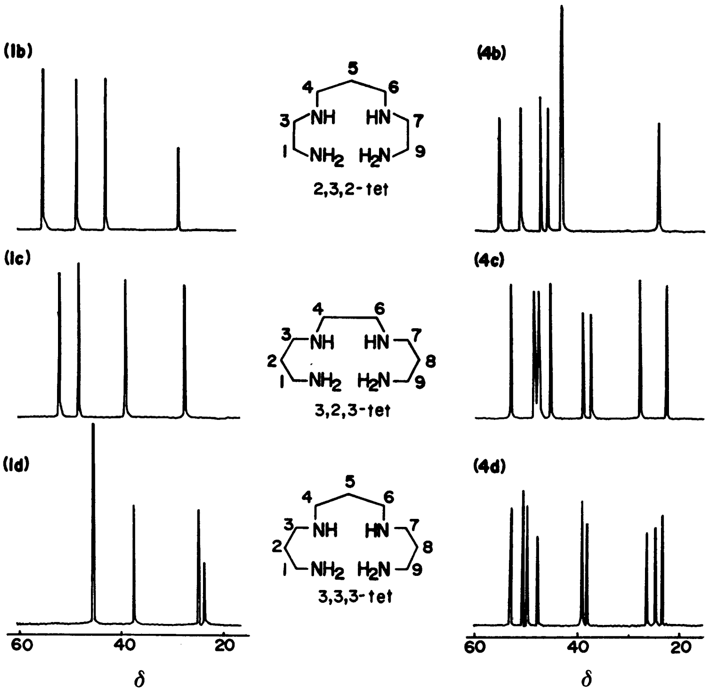
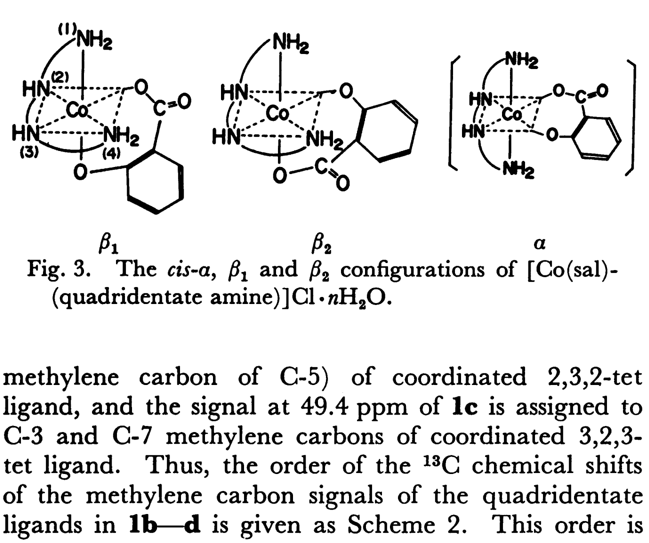
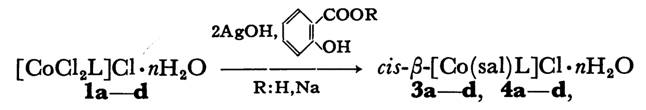


Fig. 2. The ^{13}C NMR spectra of **1b**—**d** and **4b**—**d** complexes in D_2O. (**1b**): *trans*-$[CoCl_2(2,3,2\text{-tet})]Cl\cdot2.5H_2O$. (**1c**): *trans*-$[CoCl_2(3,2,3\text{-tet})]Cl\cdot H_2O$. (**1d**): *trans*-$[CoCl_2(3,3,3\text{-tet})]Cl\cdot H_2O$. (**4b**): *cis*-$\beta_2$-$[Co(sal)(2,3,2\text{-tet})]Cl\cdot2H_2O$. (**4c**): *cis*-$\beta_2$-$[Co(sal)(3,2,3\text{-tet})]Cl\cdot3H_2O$. (**4d**): *cis*-$\beta_2$-$[Co(sal)(3,3,3\text{-tet})]Cl\cdot H_2O$.



β_1 β_2 α

Fig. 3. The *cis*-α, β_1 and β_2 configurations of $[Co(sal)(\text{quadridentate amine})]Cl\cdot nH_2O$.



$$\underset{\mathbf{1a—d}}{[CoCl_2L]Cl\cdot nH_2O} \xrightarrow[\text{R:H,Na}]{\text{2AgOH, (salicylate)}} \underset{\mathbf{3a—d},\ \mathbf{4a—d},}{cis\text{-}\beta\text{-}[Co(sal)L]Cl\cdot nH_2O}$$

	Form	L	*n*
3a		2,2,2-tet	1
3b	β_1	2,3,2-tet	1
3c		3,2,3-tet	
3d		3,3,3-tet	
4a		2,2,2-tet	1
4b	β_2	2,3,2-tet	2
4c		3,2.3-tet	3
4d		3,3,3-tet	1

methylene carbon of C-5) of coordinated 2,3,2-tet ligand, and the signal at 49.4 ppm of **1c** is assigned to C-3 and C-7 methylene carbons of coordinated 3,2,3-tet ligand. Thus, the order of the ^{13}C chemical shifts of the methylene carbon signals of the quadridentate ligands in **1b**—**d** is given as Scheme 2. This order is similar to that of ^{1}H NMR spectra. The ^{13}C NMR spectral data are collected in Table 2.

$$\begin{matrix} NH_2CH_2\underline{C}H_2NH \\ NHCH_2\underline{C}H_2NH \end{matrix} \Bigl\langle \begin{matrix} NH_2CH_2CH_2\underline{C}H_2NH \\ NHCH_2CH_2\underline{C}H_2NH \end{matrix}$$

NH-side methylene carbon

$$\Bigl\langle \begin{matrix} NH_2\underline{C}H_2CH_2NH \\ NH_2\underline{C}H_2CH_2CH_2NH \end{matrix}$$

NH_2-side methylene carbon

$$\langle NH_2CH_2\underline{C}H_2CH_2NH \langle NHCH_2\underline{C}H_2CH_2NH$$

Center methylene cabon

Scheme 2.

cis-β_1-*Salicylato(quadridentate amine)cobalt(III) Chloride Hydrate(**3a**—**d**), and* cis-β_2-*Salicylato(quadridentate amine)cobalt(III) Chloride Hydrates (**4a**—**d**)*: Complexes **3b** and **4b**—**d** have been isolated from a reaction mixture of AgOH, salicylic acid or sodium salicylate and **1b**—**d**. Salicylato(quadridentate amine)cobalt(III) complexes have three isomeric forms of *cis*-α, *cis*-β_1, and *cis*-β_2 as shown in Fig. 3. The α-form could not be obtained at pH 2—8.$^{7)}$ The separation of β_1 and β_2-forms was attempted by using ion exchange resin.$^{11,14)}$ The isolation of **3c** and **3d** from the reaction mixtures was difficult. Complexes **3b** and **4b**—**d** are soluble in water, acid solvents, DMSO and methanol, but are insoluble in the common organic solvents.

The IR spectra of **3b** and **4b**—**d** showed 4—5 absorption bands in the 3000—3300 cm^{-1} region and 6 absorption bands in the 990—1100 cm^{-1} region as

TABLE 3. SOME PHYSICAL PROPERTIES OF **3b** AND **4b—d** COMPLEXES

Complex No.	IR spectra $\tilde{\nu}$/cm^{-1} 990—1100 cm^{-1}	Absorption bands		Electric conductivity of aqueous solution
		λ/nm	ε	S cm^2 equiv.$^{-1}$
3b	1005(s), 1017(sh), 1025(vs)	333	2210[1)]	106
	1055(vs), 1070(sh), 1087(s)	530	224	
4b	1000(s), 1014(s), 1022(vs)	333	2540[1)]	98
	1036(vs), 1060(vs), 1090(vs)	525	241	
4c	1018(m), 1029(s), 1040(vs)	335	2420[1)]	100
	1048(vs), 1058(s), 1077(m)	533	217	
4d	985(m), 1028(vs), 1038(s)	335	2400[1)]	96
	1050(s), 1068(sh), 1092(m)	550	189	

Solvent: 1) H_2O.

shown in Table 3. This indicates that these complexes assume the β-form.[11,15,16]

The ^{1}H NMR spectra of **3a**, **3b**, and **4a—d** were measured in 1.8 mol dm^{-3} D_2SO_4. The signals of the center methylene protons, NH_2-side methylene protons and NH-side methylene protons of **4a—d** have been assigned by the comparison with those of **1a—d**. In complexes **4b—d**, the intensity ratio of two methylene proton signals at 2.0—2.4 and 2.2—3.2 ppm of the quadridentate ligands is 3 : 9, *i.e.*, one proton in the NH_2-side methylene protons shifts to the region (2.2—3.2 ppm) of the NH-side methylene protons. Those properties are similar to those[11,12] of **4a** (β_2-form). The methylene proton signals (2.2—3.3 ppm) of the coordinated 2,3,2-tet ligand in **3b** are similar to those of **3a** (β_1-form). Thus, the isomeric form of **3b** is *cis*-β_1-form and that of **4b—d** is *cis*-β_2-form. The signals of amine protons and salicylato protons of the coordinated ligands in **3b** and **4b—d** have been assigned by comparison with those of **3a** and **4a** complexes,[11] and are collected in Table 1. These amine proton signals disappeared in heavy water containing NaOH. In the ^{13}C NMR spectra of **4b—d** in D_2O, there have been observed 6—9 signals for the quadridentate ligands and 7 signals for the salicylato ligand. The spectrum of **4c** is similar to that of **4d** as shown in Fig. 2. The chemical shifts of the salicylato ligand in **4b—d** are similar to those of **4a**.[17] The chemical shifts of the quadridentate ligands in **4a—d** are difficult to assign to the individual carbon atoms, but regions of the chemical shifts of center methylene, NH_2-side methylene and NH-side methylene carbons are around 22—27, 37—48, and 45—55 ppm, respectively as shown in Table 2.

The absorption spectra of **4a—d** in H_2O showed two absorption bands at 333 nm (specific absorption band) and at 520—550 nm (first absorption band) as shown in Fig. 4. The ε of both the absorption bands of **4a—d** decreases with the increase of the total number of center methylene carbons of the quadridentate ligands, and their first absorption band shifts from 520 nm (**4a**) to 550 nm (**4d**) as shown in Fig. 4. In the **4a—d** complexes, their colors in the solid state are russet (**4a** and **4b**), pink-violet (**4c**) and dark-brown (**4d**). Their melting points are 240—244 °C (**4a**, **4b**), 231—233 °C (**4c**) and 190—192 °C (**4d**). Their yields of synthesis are 84% for **4a**, 61% for **4b**, 43% for **4c**, and 27% for **4d**. The *cis*-β_1 complexes of **4a** and **4b** are isolated from the reaction mixtures, but those of **4c** and **4d** could not be isolated. From the above results, the properties of **4b** are seen to be very similar to those of **4a**, though those of **4c** are similar to those of **4d**. Complex **4d** is the most unstable complex among **4a—d**. In the **3b** complex, the color (russet), melting point (≈238 °C) and yield (≈5%) are similar to those of **3a**.[11,12] These properties are attributable to the center methylenes of the quadridentate ligands. All complexes are diamagnetic. The NMR, IR, absorption spectral data and electric conductivity of the aqueous solutions are collected in Table 1—3.

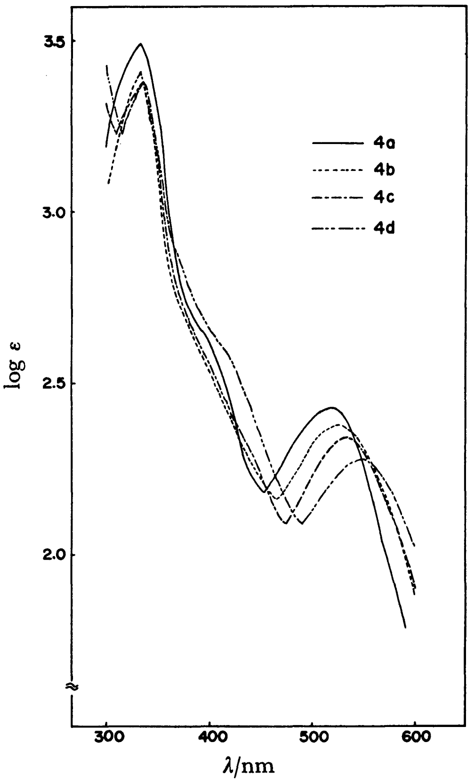


Fig. 4. The absorption spectra of **4a—d** complexes in H_2O. (**4a**): *cis*-β_2-[Co(sal)(2,2,2-tet)]Cl·H_2O. (**4b**): *cis*-β_2[Co(sal)(2,3,2-tet)]Cl·$2H_2O$. (**4c**): *cis*-β_2-[Co(sal)(3,2,3-tet)]Cl·$3H_2O$. (**4d**): *cis*-β_2-[Co(sal)(3,3,3-tet)]Cl·H_2O.

Experimental

Measurements. The NMR spectra were recorded with an FX-60 apparatus (JEOL) for ^{13}C NMR and an R-40 apparatus (Hitachi) for ^{1}H NMR. The visible absorption spectra were recorded with a Shimadzu MPS-5000 recording spectrophotometer. The magnetic susceptibilities were measured by Faraday's method using a magnetic balance (Shimadzu) at room temperature. The pH was measured with a Corning pH-meter M-125. The electric conductivity of an aqueous solution was determined by the use of a conductmetric meter, CM-30 (Shimadzu) at room temperature.

Preparation of Complexes. trans-*Dichloro(3,6-diazaoctane-1,8-diamine(trien))cobalt(III) Chloride Hydrate Hydrochloric Acid (2a) and* cis-*α-Dichloro(3,6-diazaoctane-1,8-diamine(trien))cobalt (III) Chloride (1a)* were prepared by the Sargeson's method.10,18)

trans-*Dichloro(3,7-diazanonane-1,9-diamine)cobalt(III) Chloride 2.5 Hydrate (1b) and* trans-*Dichloro(4,7-diazadecane-1,10-diamine)cobalt(III) Chloride Hydrate (1c)* were prepared by the Bosnich's method.19,20)

trans-*Dichloro(4,8-diazaundecane-1,11-diamine)cobalt(III) Chloride Hydrate (1d)*: Eighteen cubic centimeters of a methanol solution of the tetramine of 3 g (15.9 mmol) were added to 9 cm^3 of an aqueous solution of cobalt(II) chloride hexahydrate of 3.79 g (15.9 mmol). To this solution, was airated 3 h, 4.5 cm^3 of 35% hydrochloric acid was added. The solution was stirred for 1 h and concentrated in a rotary evaporator. The precipitated green complex was filtered. Acetone was added to an aqueous solution of the green complex. Then, precipitated **1c** complex was filtered and dried. Yield: 4.43 g (75.0%). Found: C, 30.06; H, 7.41; N, 15.22; Cl, 28.72%. Calcd for $CoC_9H_{26}N_4OCl_3$ (MW 371.63) C, 29.09; H, 7.05; N, 15.08; Cl, 28.62%. Mp 228—230 °C.

cis-*β_1-Salicyclato(3,7-diazanonane-1,9-diamine)cobalt(III) Chloride Hydrate (3b) and* cis-*β_2-Salicylato(3,7-diazanonane-1,9-diamine)cobalt(III) Chloride Dihydrate (4b)*: Complex 1b of 5.0 g (13.49 mmol) was added to moistened fresh AgOH, which was made from silver nitrate (4.58 g, 26.96 mmol) and potassium hydroxide (1.52 g, 27.10 mmol). The mixture was stirred in the solid state for several minutes, then 10 cm^3 of water was added to the mixture. The mixture was stirred for about 30 minutes at 60 °C, the precipitated silver chloride filtered off and washed with a small amount of water. To the reddish violet filtrate was added 1.86 g (13.47 mmol) of salicylic acid. The solution was warmed to 50 °C. The reddish brown complex thus precipitated was filtered off, washed with EtOH and acetone, dried in a desiccator over silica gel, and recrystallized from water. Separation of β_1 (**3b**) and β_2 (**4b**) form was carried out by the method described in the previous paper,11) but the length of the large column of cation-exchange resin (Dowex 50W-X2) was about 18 cm. Yields: 0.26 g (4.7%) for **3b**, 3.5 g (60.8%) for **4b**. Found **3b**: C, 41.22; H, 6.48; N, 13.51; Cl, 9.03%. Calcd for $CoC_{14}H_{26}N_4O_4Cl$ (MW 408.78) C, 41.14; H, 6.41; N, 13.71; Cl, 8.67%. Found **4b**: C, 39.13; H, 6.80; N, 13.47; Cl, 8.41%. Calcd for $CoC_{14}H_{28}N_4O_5Cl$ (MW 426.79) C, 39.40; H, 6.61; N, 13.13; Cl, 8.31%. Mp 237—239 °C for **3b**, 242—244 °C for **4b**.

cis-*β_2-Salicylato(4,7-diazadecane-1,10-diamine)cobalt(III) Chloride Trihydrate (4c)*: Complex **1c** (5.0 g, 13.98 mmol) was added to moistened fresh AgOH (3.5 g, 28.0 mmol). The mixture was stirred in the solid state for several minutes, then, 10 cm^3 of water was added to the mixture. The mixture was stirred for about 30 min at 60 °C, the precipitated silver chloride was filtered and washed with a small amount of water. To the reddish violet filtrate, sodium salicylate (2.24 g, 13.99 mmol) was added. The solution was warmed at 50 °C. The precipitated complex was filtered off, washed with EtOH and acetone, dried in a desiccator over silica gel, and recrystallized from water. Yield: 2.75 g (42.9%). Found: C, 39.41; H, 6.88; N, 12.50; Cl, 6.60%. Calcd for $CoC_{15}H_{32}N_4O_6Cl$ (MW 458.83) C, 39.27; H, 7.03; N, 12.21; Cl, 7.73%. Mp 231—233 °C.

cis-*β_2-Salicylato (4,8-diazaundecane-1,11-diamine) cobalt (III) Chloride Hydrate (4d)*: The brown complex was prepared from the reaction mixture of **1d** (5.0 g, 13.45 mmol), fresh AgOH (1.68 g, 13.46 mmol), water (about 10 cm^3), and sodium salicylate (2.08 g, 12.99 mmol) according to the preparation method of **4c**. From the brown complex, **4d** was isolated by using column chromatography of alumina. On elution with water, the bands of the complex split into four components. The complex obtained from the first band was rechromatographed with methanol eluent. The methanol solution of the first band was concentrated and dried over silica gel, the **4d** complex was recrystallized from water–acetone, twice. Yield: 1.6 g (27.2%). Found: C, 44.41; H, 7.26; N, 12.62; Cl, 7.10%. Calcd for $CoC_{16}H_{30}N_4O_4Cl$ (MW 436.83) C, 43.99; H, 6.92; N, 12.83; Cl, 8.12%. Mp 190—192 °C.

cis-*β_1-Salicylato(4,7-diazadecane-1,10-diamine)cobalt(III) Chloride (3c) and* cis-*β_1-Salicylato(4,8-diazaundecane-1,11-diamine)-cobalt(III) Chloride (3d)*: Attempts to isolate the complexes **3c** and **3d** from their reaction mixture were unsuccesful, because the bands of the **3c** and **3d** on the column of ion-exchange resin were very small.

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