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Cobalt(III) Complexes with Quadridentate Ligands. IV.[1] The Preparation and Properties of "*cis*-β_1 and β_2" Isomers of the 2-Methyl-8-quinolinolato(triethylenetetramine)-cobalt(III) and Related Complexes

Yoshihisa YAMAMOTO,* Eiko TOYOTA, and Yutaka YAMAMOTO†

Faculty of Pharmaceutical Sciences, Higashi Nippon Gakuen University, Ishikari-Tobetsu, Hokkaido 061-02

† *Tohoku College of Pharmacy, Komatsushima, Sendai 983*

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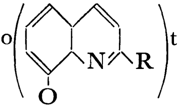
cis-β_1- and β_2-8-Quinolinolato or 2-methyl-8-quinolinolato(triethylenetetramine)cobalt(III) complexes, [Co



trien]$X_2 \cdot n H_2O$ (R: H, Me; X: Cl, NO_3), have been isolated from a reaction mixture of *cis*-α-dichloro(triethylenetetramine)cobalt(III) chloride, Ag_2O, and 8-quinolinol or 2-methyl-8-quinolinol. The separation of their *cis*-β_1 and β_2 isomers was achieved by the use of ion-exchange resin. The IR spectra of these complexes showed five or six absorption bands in the 990—1100 cm^{-1} region and four or five absorption bands in the 3000—3300 cm^{-1} region. This indicates that these complexes assume the β form. In *cis*-β_1-2-methyl-8-quinolinolato(triethylenetetramine)cobalt(III) complexes, the methyl group of the coordinated 2-methyl-8-quinolinolato ligand has a steric hindrance for the NH-side methylene protons of the coordinated trien ligand. On the other hand, no methyl group of the corresponding *cis*-β_2 form has steric hindrance for the methylene protons of the coordinated trien ligand. Therefore, the distinction of the *cis*-β_1 form and the β_2 form of these complexes has been clarified on the basis of their ^{1}H NMR spectra. Also, the ^{13}C NMR spectra of these complexes have shown two different configurations of the "*cis*-β_1 and β_2" forms.

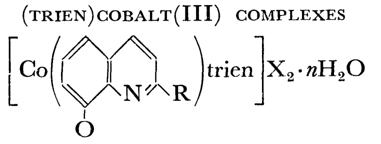
In an octahedral configuration, the isomers of bis(8-quinolinolato)metal complexes with dialkyl,[2] dichloro,[3] dicarbonyl,[4] chloro and nitrosyl,[5] diammine,[6] or ethylenediamine ligands[7] have been reported in recent years, but those of (8-quinolinolato)metal complex have not yet been described, except for the *cis*-β_1 and *cis*-β_2-8-quinolinolato(triethyleneteramine) cobalt(III) complexes.[8]

Previously, we have been concerned with the isomers (*cis*-β_1 and β_2) of salicylato(quadridentate amine) cobalt(III)chloride[9] and of 8-quinolinolato(triethylenetetramine)cobalt(III) chloride.[8] The X-ray studies of both the isomers of the above complexes and related complexes[10] have also never been described yet, because their crystals could not be obtained. Now, we have found that the methyl group of the coordinated 2-methyl-8-quinolinolato ligand in the *cis*-β_1-2-methyl-8-quinolinolato(triethylenetetramine)cobalt (III) complexes has a steric hindrance for the NH-side methylene protons of the coordinated trien ligand, though no methyl group of the corresponding *cis*-β_2 form has the steric hindrance. The present paper will, then, deal with the preparation and properties of *cis*-β_1 and β_2-2-methyl-8-quinolinolato(triethylenetetramine)cobalt(III) complexes and with the assignment of the *cis*-β_1 and β_2 isomers of their NMR spectra.

Results and Discussion

Complexes. *cis*-2-Methyl-8-quinolinolato(triethylenetetramine)cobalt(III) chloride hydrates have three isomeric forms–*cis*-β_1, *cis*-β_2, and *cis*-α, as is shown in Fig. 1. In the *cis*-β_1 form, the methyl group of the coordinated 2-methyl-8-quinolinolato ligand has a position very near the N(3)H-side methylene protons of the coordinated trien ligand, so the methyl group can show a steric hindrance for the N(3)H-side methylene protons. Thus, in the ^{1}H NMR spectra, the methylene proton signals of the coordinated trien ligand must be different from those of the corresponding 8-quinolinolato complexes. However, the methyl group in the *cis*-β_2 or *cis*-α form does not show the steric hindrance, because the methyl group has a position far from the methylene protons of the coordinated trien ligand; *i.e.*, the methylene proton signals of the coordinated trien ligand differ little from those of the corresponding 8-quinolinolato complexes in the ^{1}H NMR spectra. Then, the distinction of the *cis*-β_1 form and *cis*-β_2 form or *cis*-α form can be expected to be clarified on the basis of their NMR spectra. Thus, we have isolated the *cis*-β_1-2-methyl-8-quinolinolato(trien)cobalt(III) chloride dihydrate and the corresponding *cis*-β_2 form.

TABLE 1. THE ABBREVIATIONS OF THE 8-QUINOLINOLATO-(TRIEN)COBALT(III) COMPLEXES



$[Co(\ldots)trien]X_2 \cdot nH_2O$

No.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Form	β_1	β_1	β_2	β_2	β_1	β_1	β_2	β_2
R	H	Me	H	Me	H	Me	H	Me
X	Cl	Cl	Cl	Cl	NO_3	NO_3	NO_3	NO_3
n	2	2	2	2	1	1	1	1

The abbreviations of the 8-quinolinolato- or 2-methyl-8-quinolinolato(trien)cobalt(III) complexes studied in this paper are listed in Table 1. A mixture of *cis*-β_1 and β_2-8-quinolinolato or 2-methyl-8-quinolinolato(trien)cobalt(III) chloride dihydrate was obtained from a reaction mixture of *cis*-α-dichloro(trien) cobalt(III) chloride,[11] Ag_2O, and 8-quinolinol or 2-

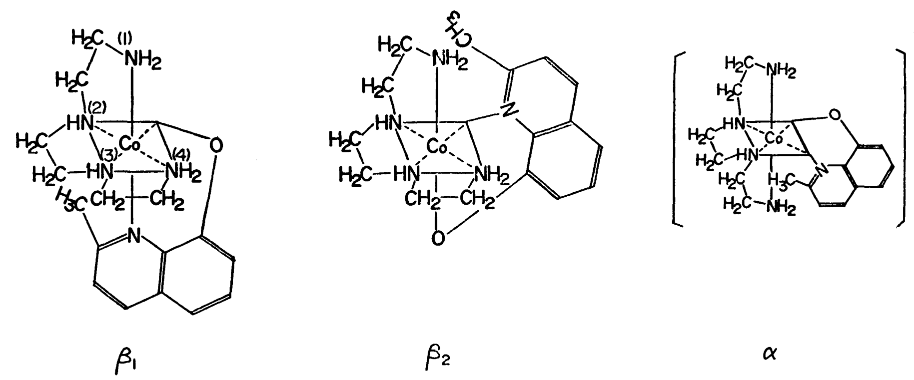


Fig. 1. The *cis*-α, β_1 and β_2 configurations of 2-methyl-8-quinolinolato(trien)cobalt(III) chloride.

TABLE 2. IR AND ABSORPTION SPECTRA OF COMPLEXES

Complex No.	IR spectra $\tilde{\nu}$/cm^{-1} 3000—3300		IR spectra $\tilde{\nu}$/cm^{-1} 990—1100		Absorption bands[1)] λ/nm	ε
1	3040(sh)	3070	1005(w)	1030	326	970
	3120(sh)	3180	1040	1060	340	1200
	3220(sh)		1070	1085	410	2590
2	3000(sh)	3020	995	1035	325	940
	3080	3200(sh)	1050	1060	342	900
			1080(sh)	1090	403	2560
3	3020(sh)	3060	1010	1035(sh)	325	1050
	3150	3200(sh)	1040	1055	339	1280
			1060(sh)		407	2690
4	3050(sh)	3090	1010(w)	1020	325	1010
	3170	3220(sh)	1040	1060	343	970
			1075(w)		409	2620
5	3050(sh)	3080	1005(w)	1030	326	1030
	3140(sh)	3200	1040	1060	340	1260
	3250(sh)		1070	1085	410	2750
6	3020(sh)	3040	1000	1040	325	1030
	3100	3210	1055	1060	342	970
			1085(sh)	1090	401	2755
7	3020(sh)	3070	1010	1040(sh)	325	1050
	3150	3200(sh)	1045	1060	339	1290
			1070(sh)		407	2755
8	3020(sh)	3070	1010	1035	324	1030
	3150	3200(sh)	1050(sh)	1060	342	990
			1075(w)		400	2690

Solvent: 1) methanol.

methyl-8-quinolinol. The separation of the *cis*-β_1 and β_2 isomers was achieved by the use of ion-exchange resin. The *cis*-α form could not be isolated from the reaction mixture at pH 2—8.[12)] From the reaction mixture of the *cis*-β_1 and β_2-8-quinolinolato or 2-methyl-8-quinolinolato(trien)cobalt(III) chloride dihydrate (**1**—**4**) and silver nitrate, the corresponding nitrate hydrates (**5**—**8**) have been prepared.

All the complexes are soluble in dimethyl sulfoxide, methanol, water, and acidic solvents, such as nitric acid, hydrochloric acid, but they are insoluble in the common organic solvents. Their β_1 forms are soluble in ethanol, though their β_2 forms are somewhat soluble in ethanol. The color in the solid state of **1** is reddish brown, **3** is yellowish brown, **2** and **5**—**7** are brown, and **4** and **8** are greyish black.

Their IR spectra showed five or six absorption bands in the 990—1100 cm^{-1} region and four or five absorption bands in the 3000—3300 cm^{-1} region, as is shown in Table 2. This indicates that they assumed the β form.[13)]

NMR Spectra. The ^{1}H NMR spectra of **1**—**8** were measured in 1.8 mol dm^{-3} D_2SO_4. The signals of the methylene and amine protons of the coordinated trien ligands in **1**—**8** were assigned on the basis of the results in the previous papers.[9,10)] The methylene protons of the coordinated trien ligand in **1** showed one signal, though those of the coordinated trien ligand in **3** showed two signals, in the 2.4—4.0 ppm region, as is shown in Table 3 and Fig. 2. The differences between **1** and **3** are similar to those between *cis*-β_1 and β_2-salicylato(trien)cobalt(III) chloride hydrate,[10)] *cis*-β_1- and β_2-[Co(sal)trien]Cl·H_2O (**9**); therefore, the **1** and **3** complexes can be assigned to the *cis*-β_1 form

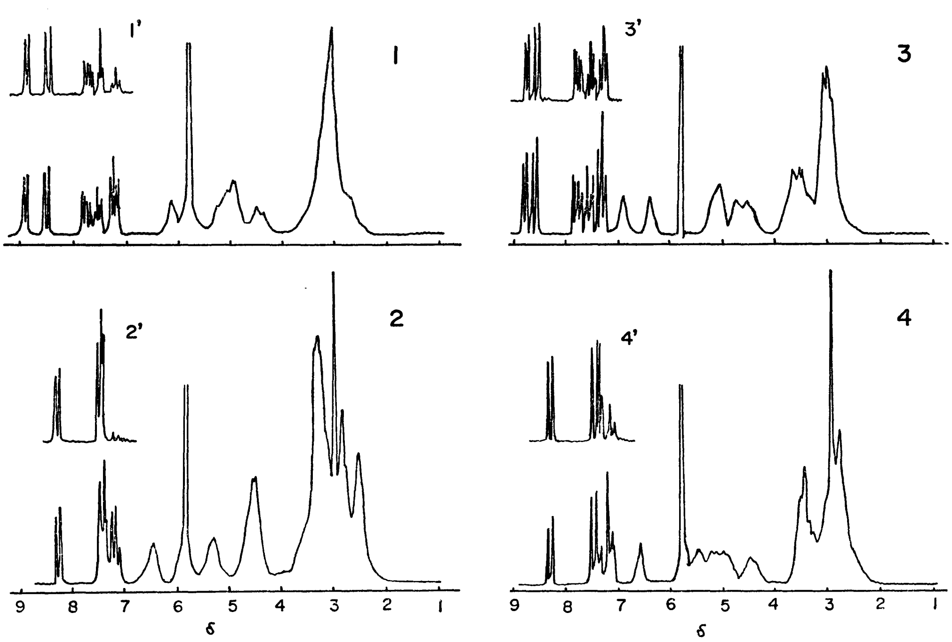


Fig. 2. The ^{1}H NMR spectra of **1**—**4** complexes.
1: *cis*-β_1-[Co(8-quinolinolato)trien]Cl$_2\cdot$2H$_2$O; 2: *cis*-β_1-[Co(2-methyl-8-quinolinolato)trien]Cl$_2\cdot$2H$_2$O; 3: *cis*-β_2-[Co(8-quinolinolato)trien)Cl$_2\cdot$2H$_2$O; 4: *cis*-β_2-[Co(2-methyl-8-quinolinolato)-trien]Cl$_2\cdot$2H$_2$O in 1.8 mol dm^{-3} D$_2$SO$_4$.
The signals of **1'**—**4'** are those in the 1.8 mol dm^{-3} D$_2$SO$_4$ solution after 25 min.

and *cis*-β_2 form respectively. In the ^{1}H NMR spectra of the **2** and **4** complexes, the methylene protons of **2** show three signals, and the intensity ratios are 2:2:8 in the 2.5—3.8 ppm region. These signals are different from those (one signal) of **1**, as is shown in Fig. 2. On the other hand, the methylene proton signals of **4** are little different from those of **3**. Therefore, the isomeric forms of **2** and **4** have been assigned to the *cis*-β_1 and *cis*-β_2 forms respectively.

In the **3** and **4** complexes, the signals at 2.2—3.2 ppm (8H) and 3.2—4.0 ppm (4H) have been assigned to the NH-side methylene protons and the NH$_2$-side methylene protons of the coordinated trien ligand respectively. The chemical shift of the NH-side methylene protons of the **3** and **4** complexes is at a higher field than that of the NH$_2$-side methylene protons. This property is different from that of **9**.[9] This can be attributed to the electronic and structural effects of the coordinated 8-quinolinolato and salicylato ligands. On the other hand, the signals of the amine protons of the coordinated trien ligand in **2** and **4** are different from those of **1** and **3**. This can be based on the electronic effect of the methyl group of the coordinated 2-methyl-8-quinolinolato ligand in the **2** and **4** complexes. The NMR spectral data of the nitrate complexes (**5**—**8**) are similar to those of the chloride complexes (**1**—**4**), as is shown in Table 3.

In the ^{1}H NMR spectra of **1**—**4**, both the ring proton signals (H-5 and H-7) of the coordinated 8-quinolinolato or 2-methyl-8-quinolinolato ligand changed to the proton signals of **1'**, **2'**, **3'**, and **4'** after 25 min, as is shown in Fig. 2. Then, both the ring protons were replaced at deuterium in a 1.8 mol dm^{-3} D$_2$SO$_4$ solution. The order of the replacement is: **3**<**1**<**4**<**2**. Thus, the deuterium replacement of the *cis*-β_1

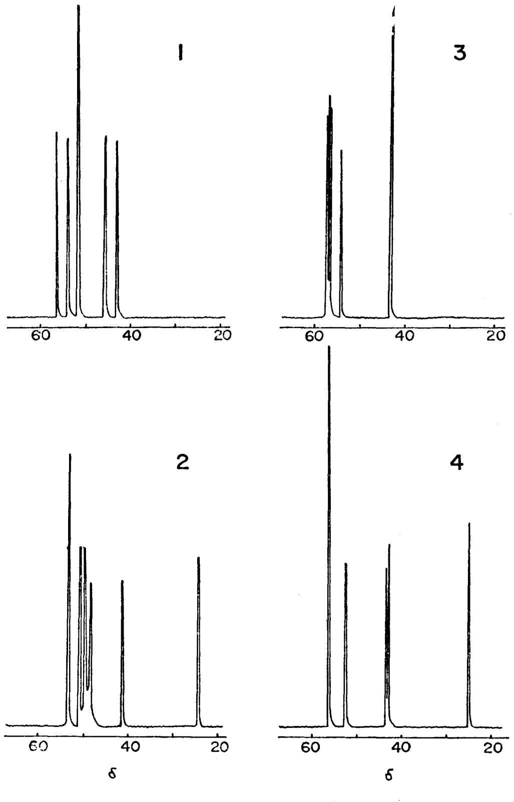


Fig. 3. The ^{13}C NMR spectra of **1**—**4** complexes in D$_2$O.
1: *cis*-β_1-[Co(8-quinolinolato)trien]Cl$_2\cdot$2H$_2$O; 2: *cis*-β_1-[Co(2-methyl-8-quinolinolato)trien]Cl$_2\cdot$2H$_2$O; 3: *cis*-β_2-[Co(8-quinolinolato)trien]Cl$_2\cdot$2H$_2$O; 4: *cis*-β_2-[Co(2-methyl-8-quinolinolato)trien]Cl$_2\cdot$2H$_2$O.

TABLE 3. ^{1}H AND ^{13}C NMR

^{1}H	$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$ δ					
Complex (Form)	$-C\mathbf{H}_2NHC\mathbf{H}_2CH_2NH_2$	$NHCH_2C\mathbf{H}_2NH_2$	$N(1)H_2$	$N(4)H_2$	$N(3)H$	$N(2)H$
1 (β_1)	2.42—3.76(12H)		4.48(1H)4.69—5.37(3H)		a)	6.14(1H)
2 (β_1)	2.51(2H)2.81(2H)3.03—3.80(8H)		4.52(3H)	5.31(1H)	a)	6.45(1H)
3 (β_2)	2.39—3.24(8H)	3.24—4.01(4H)	4.43(1H)4.64(1H)	5.06(2H)	6.37(1H)	6.87(1H)
4 (β_2)	2.27—3.22(8H)	3.22—3.78(4H)	4.47(1H)4.70—5.36(2H)	5.50(1H)	a)	6.60(1H)
5 (β_1)	2.43—3.76(12H)		4.44(1H)4.72—5.36(3H)		a)	6.13(1H)
6 (β_1)	2.51(2H)2.82(2H)3.03—3.91(8H)		4.53(3H)	5.29(1H)	5.93(1H)	6.39(1H)
7 (β_2)	2.42—3.27(8H)	3.27—4.03(4H)	4.46(1H)4.68(1H)	5.02(2H)	6.31(1H)	6.82(1H)
8 (β_2)	2.20—3.22(8H)	3.22—3.82(4H)	4.47(1H)4.75—5.32(2H)	5.49(1H)	a)	6.61(1H)

^{13}C	$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$ δ						(2-Methyl-)			
	$NHCH_2\mathbf{C}H_2NH_2$		$-\mathbf{C}H_2NH\mathbf{C}H_2CH_2NH_2$				C-2	C-3	C-4	C-5
1 (β_1)	43.4	46.1	52.1	54.5	56.5		150.1	114.9	141.3	124.0
2 (β_1)	41.5	48.4	49.5	50.9	53.5		164.3	114.7	140.8	127.8
3 (β_2)	43.3		54.1	56.7	56.8	57.2	151.5	115.1	141.0	124.2
4 (β_2)	43.1	43.6	52.4	56.3			163.9	115.2	141.0	127.0
L							156.9	109.8	136.1	122.7

Solvent and standard: 1) 1.8 mol dm^{-3} D_2SO_4, internal DSS, 2) D_2O, internal dioxane (δ=67.4), 3) $CDCl_3$, internal $CDCl_3$ (δ=77.1). a): This signal overlapped with each solvent. **L**: 2-methyl-8-quinolinol.

form is faster than that of the *cis*-β_2 form. In both *cis*-β_1 and β_2 complexes, that of the 2-methyl-8-quinolinolato complexes is faster than that of the 8-quinolinolato complexes.

In the ^{13}C NMR spectra of the **1**—**4** complexes in D_2O, there have been observed four or five signals for the coordinated trien ligand and nine or ten signals for the coordinated 8-quinolinolato or 2-methyl-8-quinolinolato ligands. From Fig. 3, it can be seem that the spectrum of **4** is very similar to that of **3**, but the spectrum of **2** is different from that of **1** because of the steric hindrance of the methyl group. These results also suggest that the **3** and **4** complexes are *cis*-β_2 form, while the **1** and **2** complexes are *cis*-β_1 form. The chemical shifts of the coordinated 8-quinolinolato or 2-methyl-8-quinolinolato ligands[7] in **1**—**4** are assigned; they are collected in Table **3**. The carbon signals of C-2 of the coordinated 2-methyl-8-quinolinolato ligands in the **2** and **4** complexes shift to a low field. This is the effect of the methyl group[14] of the coordinated 2-methyl-8-quinolinolato ligand. The chemical shifts of the coordinated trien ligand in **1**—**4** are difficult to assign to the individual carbon atom, though they are collected in the two groups[9] of the NH-side methylene carbons and the NH_2-side methylene carbons.

Other Properties. The absorption spectra of **1**—**8** have three absorption bands around 325, 340, and 400 nm in methanol as is shown in Table 2. The absorption bands at 340 nm of the **1**, **3**, **5**, and **7** complexes are stronger than those at 325 nm, though the absorption bands at 340 nm of the **2**, **4**, **6**, and **8** complexes are weaker than those at 325 nm, as is shown in Table 2. This property is based on the substituted methyl group in the coordinated 8-quinolinolato ligand. The absorption bands around 400 nm are charge-transfer bands.[6,7] All the complexes are diamagnetic, and their electric conductivities in an aqueous solution are 225—250 S cm^2 equiv.$^{-1}$

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 a IR-27G spectrophotometer (Shimadzu). The visible absorption spectra were recorded with a Shimadzu MPS-5000 recording spectrophotometer. The electric conductivities of an aqueous solution were determined by the use of a conductmetric meter, CM-30 (Shimadzu), at room temperature. The pH was measured with a Corning pH-meter M-125. The magnetic susceptibilities were measured by Faraday's method using a magnetic balance (Shimadzu) at room temperature.

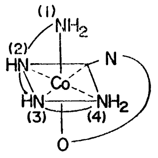
Preparation of Complexes. *cis-β-8-Quinolinolato(trien)cobalt(III) Chloride Dihydrate (**A**) and cis-β-2-Methyl-8-quinolinolato(trien)cobalt(III) Chloride Dihydrate (**B**)*: A methanol solution (100 cm^3) of 8-quinolinol (4.35 g, 30 mmol) (or 2-methyl-8-quinolinol (4.78 g, 30 mmol)) was added, drop by drop, to an aqueous solution (100 cm^3) of $[CoCl(OH)\text{-}trien]^+$,[15] which had been prepared from *cis*-α-dichloro-(trien)cobalt(III) chloride[11] (9.35 g, 30 mmol), and Ag_2O, which had been prepared from $AgNO_3$ (5.1 g, 30 mmol) and KOH (1.69 g, 30.1 mmol). The mixture was then stirred for 30 h at 50 °C. In the reaction, *cis*-α-dichloro-(trien)cobalt(III) chloride isomerized to the corresponding β form. The reaction mixture was then concentrated on a rotary evaporater and dried over silica gel. Complex **A** (or **B**) was extracted with methanol from the dried mixture and was recrystallized from water. Yields: 6.10 g (44.6%) for **A**; 6.51 g (46.1%) for **B**.

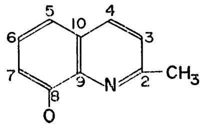
*Separation of cis-β_1-8-Quinolinolato(trien)cobalt(III) Chloride Dihydrate (**1**), cis-β_1-2-Methyl-8-quinolinolato(trien)cobalt(III)*

SPECTRA OF COMPLEXES

(2-Methyl-)8-quinolinolato δ							
H-5	H-7	H-6	H-3	H-4	H-2	CH_3	Solvent
7.22 d	7.26 d	7.51 dd	7.75 dd	8.52 d	8.92 d	—	1
7.00—7.27(2H)		7.27—7.51(2H)		8.24 d	—	2.98(s, 3H)	1
7.16—7.36(2H)		7.51 dd	7.74 dd	8.54 d	8.73 d	—	1
7.05—7.28(2H)		7.28—7.60(2H)		8.30 d	—	2.96(s, 3H)	1
7.21 d	7.23 d	7.49 dd	7.74 dd	8.52 d	8.91 d	—	1
7.00—7.30(2H)		7.31—7.52(2H)		8.25 d	—	2.96(s, 3H)	1
7.15—7.36(2H)		7.50 dd	7.72 dd	8.52 d	8.70 d	—	1
7.07—7.30(2H)		7.30—7.58(2H)		8.30 d	—	2.98(s, 3H)	1

8-quinolinolato δ						
C-6	C-7	C-8	C-9	C-10	CH_3	
115.9	131.2	146.5	165.1	131.4	—	2
116.3	129.9	146.2	164.6	129.4	24.7	2
116.5	131.4	145.9	164.6	131.4	—	2
116.6	129.8	145.3	164.5	129.9	25.1	2
117.6	126.7	137.7	151.8	126.7	24.9	3





Chloride Dihydrate (2), cis-β_2-8-Quinolinolato(trien)cobalt(III) Chloride Dihydrate (3), and cis-β_2-2-Methyl-8-quinolinolato-(trien)cobalt(III) Chloride Dihydrate (4): Five-tenths of a gram of *cis*-β-[Co(oxine-R)trien]$Cl_2 \cdot 2H_2O$ (R: H, CH_3) was dissolved in 1.5 cm^3 of water, after which the solution was passed through a large column of cation-exchange resin (2.5×30 cm, SP-Sephadex C-25, Na^+ form). Two bands separated on subsequent elution with a 0.2 mol dm^{-3} Na_2SO_4 solution. Solutions of the first band (β_2 complex) and of the second band (β_1 complex) were concentrated in a rotary evaporator, and the Na_2SO_4 was removed by filtration. The *cis*-β_1 and β_2 complexes were recrystallized from water-acetone twice. Yields: 0.05 g (10.0%) for **1**; 0.04 g (8.0%) for **2**; 0.42 g (84.0%) for **3**; 0.41 g (82.0%) for **4**. Found **1**: C, 39.78; H, 6.48; N, 15.20; Cl, 15.50%. **2**: 40.48; H, 6.72; N, 14.84; Cl, 14.86%. **3**:C, 39.47; H, 6.29; N, 15.13; Cl, 15.30%. **4**: C, 40.79; H, 6.33; N, 14.87; Cl, 15.12%. Calcd for **1** and **3**: $CoC_{15}H_{28}N_5O_3Cl_2$ (MW 456.26), C, 39.49; H, 6.19; N, 15.35; Cl, 15.54%. **2** and **4**: $CoC_{16}H_{30}N_5O_3Cl_2$ (MW 470.29) C, 40.86; H, 6.43; N, 14.89; Cl, 15.08%. Mp (or Decomp) **1**: (237—238 °C), **2**: 211—213 °C, **3**: (241—243 °C), **4**: 213—215 °C. Λ=250 for **1**, 230 for **2**, 240 for **3**, and 225 S cm^2 equiv.$^{-1}$ for **4** in water.

cis-β_1-8-Quinolinolato(trien)cobalt(III) Nitrate Hydrate (5) and cis-β_2-8-Quinolinolato(trien)cobalt(III) Nitrate Hydrate (7): To an aqueous solution of Complex **1** or **3** (0.5 g, 1.10 mmol) we added an aqueous solution of silver nitrate (0.38 g, 2.24 mmol). The mixture was then stirred, and the silver chloride thus precipitated was filtered. The filtrate was concentrated. Complexes **5** and **7** were recrystallized from water twice. Yields: 0.46 g (85.2%) for **5**, 0.48 g (88.9%) for **7**. Found **5**: C, 36.96; H, 5.04; N, 20.25%. **7**: C, 37.23; H, 5.22; N, 19.72%. Calcd for $CoC_{15}H_{26}N_7O_8$ (MW 491.35) C, 36.67; H, 5.33; N, 19.95%.

cis-β_1-2-Methyl-8-quinolinolato(trien)cobalt(III) Nitrate Hydrate (6) and cis-β_2-2-Methyl-8-quinolinolato(trien)cobalt(III) Nitrate Hydrate (8): These complexes were prepared from Complex **2** or **4** (0.5 g, 1.06 mmol) and silver nitrate (0.36 g, 2.12 mmol) according to the method used for Complexes **5** and **7**. Yields: 0.4 g (74.6%) for **6**, 0.42 g (78.4%) for **8**. Found **6**: C, 38.71; H, 5.18; N, 19.49%. **8**: C, 37.67; H, 5.38; N, 19.91%. Calcd for $CoC_{16}H_{28}N_7O_8$ (MW 505.38) C, 38.03; H, 5.58; N, 19.40%.

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