

The Preparation and Properties of Ethylenediamine(8-quinolinolato)cobalt(III) Complexes

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Bis(ethylenediamine)(8-quinolinolato)cobalt(III) chloride dihydrate and ethylenediaminebis(8-quinolinolato)-cobalt(III) chloride dihydrate have been isolated and characterized. The ^1H -NMR spectrum of the latter complex indicates that the two oxygen atoms of the coordinated 8-quinolinolato ligands are in the *cis* positions.

Previously, we have reported the preparation and properties of the ammine(8-quinolinolato)cobalt(III) complexes.¹⁾ Among these complexes, the two oxygen atoms of the coordinated 8-quinolinolato ligands of diamminebis(8-quinolinolato)cobalt(III) chloride hydrate were found to be in the *trans* positions.

In the corresponding ethylenediamine complexes which have been obtained in the present research, the two oxygen atoms of the coordinated 8-quinolinolato ligands were found to be in the *cis* positions.

Results and Discussion

Bis(ethylenediamine)(8-quinolinolato)cobalt(III) chloride dihydrate, $[\text{Co}(\text{oxine})_2(\text{en})_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (**1**)

and ethylenediaminebis(8-quinolinolato)cobalt(III) chloride dihydrate, $[\text{Co}(\text{oxine})_2(\text{en})]\text{Cl} \cdot 2\text{H}_2\text{O}$ (**2**)

have been obtained by the chromatographic separation of the reaction mixture of *trans*- or *cis*-dichlorobis(ethylenediamine)cobalt(III) chloride,²⁾ Ag_2O and 8-quinolinol. Tris(8-quinolinolato)cobalt(III) complex^{3,4)} (**3**) and tris(ethylenediamine)cobalt(III) chloride⁵⁾ (**4**) are produced as by-products from the reaction mixture. Complex **1** is very soluble in water, soluble in methanol and slightly soluble in ethanol. Complex **2** is soluble in methanol and somewhat soluble in water and ethanol. These complexes are insoluble in most other organic

solvents. The corresponding nitrate (**5**) has been prepared from the chloride (**1**) and silver nitrate. Also the corresponding picrate (**6**) has been prepared from the chloride (**2**) and picric acid. The possible geometrical structures of **2** are shown in Fig. 1. The NMR spectra and behavior in chromatography with Dowex 50W-X2^{6,7)} show that the complex **2** obtained has one of these structures and is not a mixture of isomers.

The absorption bands of 8-quinolinolato-metal complexes have already been reported by several researchers.^{8–10)} The absorption spectra of **1** and **2** have three absorption bands around 324, 338, and 407 nm in methanol. The bands around 407 nm are considered to be charge-transfer bands.¹⁾ These bands shift to 383–388 nm in water.

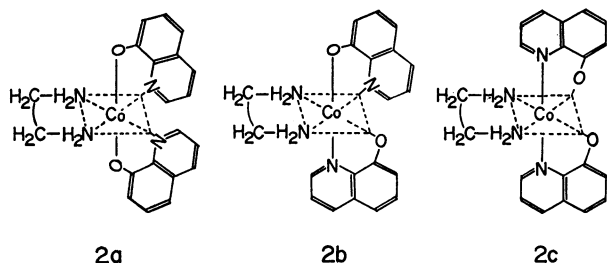


Fig. 1. The possible isomeric structures of $[\text{Co}(\text{oxine})_2(\text{en})]\text{Cl} \cdot 2\text{H}_2\text{O}$.

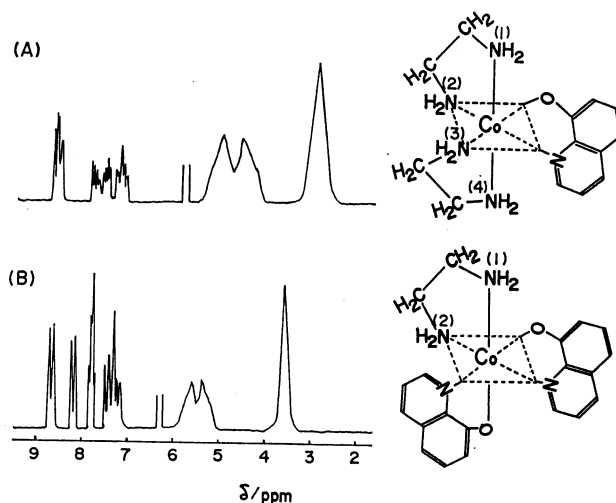


Fig. 2. The ^1H -NMR spectra of ethylenediamine-(8-quinolinolato)cobalt(III) chloride.

(A): $[\text{Co}(\text{oxine})(\text{en})_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ in 1.8 mol dm^{-3} D_2SO_4 , (B): $[\text{Co}(\text{oxine})_2(\text{en})]\text{Cl} \cdot 2\text{H}_2\text{O}$ in 2.5 mol dm^{-3} D_2SO_4

In the ^1H -NMR spectrum of **1** shown in Fig. 2, the signal at 2.92 ppm is assigned to the methylene protons of the coordinated ethylenediamine. The NH_2 protons of that ligand showed two singlet signals in the intensity ratio of 1 : 1. The singlet signal at 4.55 ppm (4H) is assigned to the protons of the two amines of $\text{N}(1)\text{H}_2$ and $\text{N}(4)\text{H}_2$ which are *cis*¹⁾ to the coordinated 8-quinolinolato ligand, while the singlet signal at 5.0 ppm (4H) is assigned to the protons of $\text{N}(2)\text{H}_2$ and $\text{N}(3)\text{H}_2$ which are *trans* to the coordinated 8-quinolinolato ligand. In

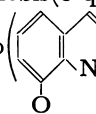
† Present address: Takeda Chemical Industries Ltd., 27 Dosho-machi 2-chome, Higashi-ku, Osaka 541.

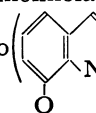
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TABLE 1. ¹H-NMR SPECTRA OF ETHYLENEDIAMINE(8-QUINOLINOLATO)COBALT(III) COMPLEXES

Complex No.	NH ₂ CH ₂ CH ₂ NH ₂ δ/ppm					8-Quinolinolato δ/ppm	Picrate δ/ppm	Solvent and standard
	CH ₂	N(4)H ₂	N(1)H ₂	N(2)H ₂	N(3)H ₂			
1	2.92 s(8H)	4.55 s(4H)		5.0 s(4H)		7.0—8.7 m(6H)		A-1
5	2.99 s(8H)	4.55 s(4H)		5.0 s(4H)		7.1—8.7 m(6H)		A-1
2	3.54 s(4H)		5.38 s(2H)	5.58 s(2H)		7.1—8.7 m(12H)		B-1
6	2.78 s(4H)		5.31 s(2H)	5.80 s(2H)		7.0—8.4 m(12H)	8.6 s(2H)	C-2
L						6.7—8.7 m		D-2

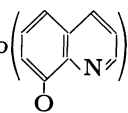
Solvents: A, 1.8 mol dm⁻³ D₂SO₄; B, 2.5 mol dm⁻³ D₂SO₄; C, DMSO-*d*₆; D, CDCl₃. Standard: 1, internal DSS; 2, internal TMS.

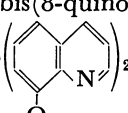
the ¹H-NMR spectrum of **2**, the signal (3.54 ppm) at the highest field is assigned to the methylene protons of the coordinated ethylenediamine. The NH₂ protons of that ligand showed two singlet signals in the intensity ratio of 1 : 1. The singlet signal at 5.38 ppm is assigned to the protons of N(1)H₂ which are *trans*^{11,12} to the oxygen of the coordinated 8-quinolinolato ligand. Another singlet signal at 5.58 ppm is assigned to the protons of N(2)H₂ group which are *trans* to the nitrogen of that ligand, which is less electronegative than the 8-quinolinol oxygen. Thus, the structure of **2** is considered to be **2b**. The two oxygen atoms of the coordinated 8-quinolinolato ligands in **2b** are in the *cis* positions in contrast to most of the known cases where the two oxygen atoms of the coordinated 8-quinolinolato ligands in an octahedral configuration are in *trans*¹³⁻¹⁵ positions. The diamminebis(8-quinolinolato)cobalt(III) chloride dihydrate, [Co()₂(NH₃)₂]Cl·H₂O (**7**),

reported previously,¹ is included among these cases. The complexes of **1**, **2**, **7**, and tetraammine(8-quinolinolato)cobalt(III) chloride monohydrate, [Co()(NH₃)₄]Cl₂·H₂O (**8**),¹ are thermally

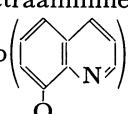
stable compounds. Concerning decomposition of these complexes, their stabilities are arranged in the following order: **1** (247 °C), **7** (205 °C), **8** (177 °C), **2** (163 °C).

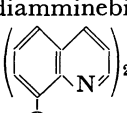
The ethylenediamine complex (**2**) is less stable than the corresponding ammine complex (**7**) and bis(ethylenediamine) complex (**1**). This is probably due to the positions of the two oxygen atoms of the coordinated 8-quinolinolato ligands of **2** in an octahedral configuration; in the ammine complexes, diammine complex **7** is more stable than the tetraammine complex (**8**). Tetraammine-

(8-quinolinolato)cobalt(III) nitrate, [Co()]-

(NH₃)₄](NO₃)₂ (**9**), and diamminebis(8-quinolinolato)-cobalt(III) nitrate hydrate, [Co()₂(NH₃)₂]-

NO₃·H₂O (**10**) have been prepared from the corresponding chloride¹ and silver nitrate. Also tetraammine-

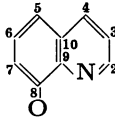
(8-quinolinolato)cobalt(III) picrate, [Co()]-

(NH₃)₄](pic)₂ (**11**) and diamminebis(8-quinolinolato)-cobalt(III) picrate, [Co()₂(NH₃)₂]pic (**12**)

have been prepared from the corresponding chloride¹ and picric acid. ¹H-NMR spectral data of **1**, **2**, **5**, and **6** complexes are listed in Table 1.

In the ¹³C-NMR spectra of **1** and **2** in D₂O, nine

TABLE 2. ¹³C-NMR SPECTRA OF THE AMINE(8-QUINOLINOLATO)COBALT(III) COMPLEXES

Complex No.	NH ₂ CH ₂ CH ₂ NH ₂ δ/ppm				<div><div></div><div>δ/ppm</div></div>										Solvent and standard
	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10						
1	44.1	45.0	45.8	46.2	150.3	115.0	141.0	124.1	116.3	131.3	146.2	165.1	131.3	a	
2		45.9			148.5	114.7	139.6	123.4	116.2	131.1	145.5	165.3	130.7	a	
7					149.1	111.0	138.1	122.7	114.4	129.7	d	166.6	130.2	b	
8					150.2	115.2	140.9	124.0	116.6	131.2	146.0	164.8	131.2	a	
3					146.1	111.0	137.8	121.5	115.4	130.3		167.2	130.3	c	
					147.0	111.2	137.9	122.1	116.0	130.7	d	168.0	130.7		
						111.8	138.2		116.3	131.1		169.3	131.1		
L					147.9	110.3	136.1	121.7	117.9	127.7	138.3	152.4	128.6	c	

Solvent and standard: a; D₂O, internal dioxane (δ=67.4 ppm). b; DMSO-*d*₆ (δ=39.5 ppm). c; CDCl₃ (δ=77.1 ppm). L: 8-Quinolinol, d: disappeared.

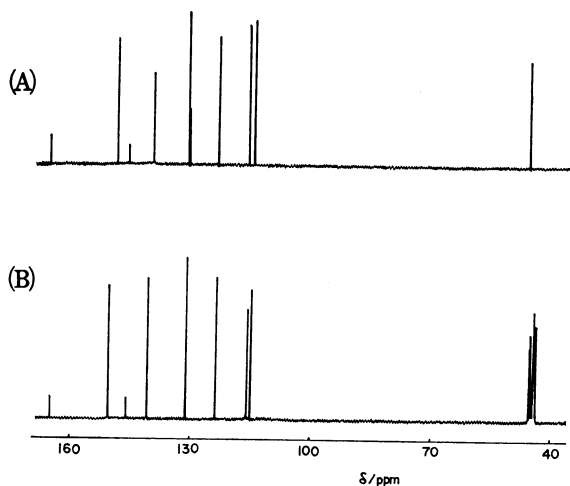


Fig. 3. The ^{13}C -NMR spectra of ethylenediamine-(8-quinolinolato)cobalt(III) chloride.

(A): $[\text{Co}(\text{oxine})_2(\text{en})]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ in D_2O , (B): $[\text{Co}(\text{oxine})(\text{en})_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ in D_2O .

signals have been observed for the coordinated 8-quinolinolato ligand in the regions 115–170 ppm. The assignment (Table 2) of that ligand has been tried by the means of a consideration of the assignments of quinoline¹⁶ and 8-quinolinol. The chemical shifts of C-8 of quinoline move to lower field upon the substitution of a hydroxyl group¹⁷ to form 8-quinolinol. The methylene carbons of the coordinated ethylenediamine in **1** have been observed at 44.1, 45.0, 45.8, and 46.2 ppm and those of **2** have been observed at 45.9 ppm as is shown in Fig. 3, but the chemical shifts of the methylene carbons of the coordinated ethylenediamine of **1** are difficult to assign to the individual carbon atom. The methylene carbon signals of **2** overlapped. An X-ray study is expected to give further information as to the structure of **2b** or **2c**.

The complexes **1**, **2**, **5**–**12** are diamagnetic compounds.

Experimental

Measurements. The NMR spectra were recorded with an FX-60 spectrometer (JEOL) for ^{13}C -NMR and R-40 (Hitachi) for ^1H -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 electric conductivities of aqueous solutions were determined by the use of a conductometer, CM-30 (Shimadzu) at room temperature.

Preparation of Complexes. *Bis(ethylenediamine)(8-quinolinolato)cobalt(III) Chloride Dihydrate (1)*, and *Ethylenediaminebis(8-quinolinolato)cobalt(III) Chloride Dihydrate (2)* and *Tris(8-quinolinolato)cobalt(III) Complex (3)* and *Tris(ethylenediamine)cobalt(III) Chloride (4)*: One hundred cubic centimeters of a methanol solution of 8-quinolinol (4.16 g, 28.66 mmol) were slowly added to 100 cm^3 of an aqueous solution of $[\text{Co}(\text{OH})_2(\text{en})_2]^+$, which was prepared from *trans*- $[\text{CoCl}_2(\text{en})_2]\text{Cl}$ (4.0 g, 14.01 mmol) and Ag_2O which, in turn, was prepared from AgNO_3 (4.8 g, 28.26 mmol) and KOH (2.0 g, 35.65 mmol). They were stirred for 2 d at 60 $^\circ\text{C}$. The precipitated yellow complex (**3**) was filtered. The filtrate was concentrated on a rotary evaporator and dried

over silica gel. Complex **2** was extracted with dry ethanol from the dried reaction mixture. The purification (removal of **1**) of **2** from the ethanol solution was achieved by column chromatography on alumina. On elution with ethanol–acetone (3 : 1), the first band (complex **2**) was collected and concentrated. Complex **2** was recrystallized from ethanol–ether twice. Complex **1** was extracted with dry methanol from the dried reaction mixture. This complex was recrystallized from water–acetone twice. Complex **4** remaining to the last did not dissolve in dry methanol. Yield: 0.8 g (13.27%) for **1**, 2.9 g (43.23%) for **2**, 1.2 g (17.4%) for **3** and 0.5 g (10.3%) for **4**. Found **1**: C, 36.51; H, 6.19; N, 16.70; Cl, 16.98%. **2**: C, 49.95; H, 5.20; N, 11.39; Cl, 7.41%. Calcd for **1**: $\text{CoC}_{13}\text{H}_{26}\text{N}_5\text{O}_3\text{Cl}_2$ (M.W. 430.22) C, 36.29; H, 6.09; N, 16.28; Cl, 16.48%. **2**: $\text{CoC}_{20}\text{H}_{24}\text{N}_4\text{O}_4\text{Cl}$ (M.W. 478.82) C, 50.17; H, 5.05; N, 11.70; Cl, 7.40%. Dec 245–247 $^\circ\text{C}$ for **1**, 161–163 $^\circ\text{C}$ for **2**. $\lambda = 270 \text{ S cm}^2$ for **1**, 130 S cm^2 for **2** in water. Absorption spectra, 320 nm ($\epsilon = 910$), 335 (1100), and 338 (2400) in water, 271 nm ($\epsilon = 11000$), 324 (1150), 338 (1250), and 407 (2900) in methanol for **1**, 320 nm ($\epsilon = 1070$), 334 (1370), and 384 (4780) in water, 267 nm ($\epsilon = 14800$), 325 (2400), 339 (2960), and 404 (5730) in methanol for **2**. Color: brick-red for **1**, brown for **2**.

Bis(ethylenediamine)(8-quinolinolato)cobalt(III) Nitrate, $[\text{Co}(\text{8-quinolinolato})_2(\text{en})_2](\text{NO}_3)_2$ (**5**): To an aqueous solution of **1**

(0.5 g, 1.16 mmol) was added an aqueous solution of silver nitrate (0.4 g, 2.35 mmol). The mixture was stirred, and the silver chloride precipitated was filtered. The filtrate was concentrated and recrystallized from water twice. Yield: 0.42 g (80.9%). Found: C, 34.91; H, 5.17; N, 21.43%. Calcd for $\text{CoC}_{13}\text{H}_{22}\text{N}_7\text{O}_7$ (M.W. 447.30) C, 34.91; H, 4.96; N, 21.92%. Dec 245–249 $^\circ\text{C}$. Absorption spectrum: 322 nm ($\epsilon = 860$), 339 (1050) and 388 (2500) in water. Color: brick-red.

Ethylenediaminebis(8-quinolinolato)cobalt(III) Picrate, $[\text{Co}(\text{8-quinolinolato})_2(\text{en})_2]\text{pic}$ (**6**): An aqueous solution of **2** (0.30 g,

0.63 mmol) was added to a solution of picric acid (0.16 g, 0.7 mmol), the mixture was stirred, and the separated brown complex was filtered and recrystallized from methanol. Yield: 0.29 g (66.2%). Found: C, 48.76; H, 3.92; N, 15.50%. Calcd for $\text{CoC}_{26}\text{H}_{22}\text{N}_7\text{O}_9$ (M.W. 635.44) C, 49.14; H, 3.49; N, 15.43%. Dec 156–160 $^\circ\text{C}$. Absorption spectrum: 267 nm ($\epsilon = 18300$), 350 sh (15400), 362 (15700), and 393 (15100) in methanol. Color: brown.

Tetraammine(8-quinolinolato)cobalt(III) Nitrate (9). An aqueous solution of silver nitrate (0.90 g, 5.30 mmol) was added to an aqueous solution of tetraammine(8-quinolinolato)cobalt(III) chloride dihydrate¹ (**8**) (1.0 g, 2.78 mmol). The mixture was stirred, and the precipitated silver chloride was filtered. The filtrate was concentrated and recrystallized from water twice. Yield: 0.92 g (83.7%). Found: C, 27.29; H, 4.87; N, 24.44%. Calcd for $\text{CoC}_9\text{H}_{18}\text{N}_7\text{O}_7$ (M.W. 395.22) C, 27.35; H, 4.59; N, 24.81%. Dec 163–165 $^\circ\text{C}$. $\lambda = 240 \text{ S cm}^2$ in water. Absorption spectrum: 321 nm ($\epsilon = 940$), 337 (1170), and 384 (2450) in water. ^1H -NMR spectrum,¹⁾ δ : 3.36 ppm (s, 6H) for $\text{N}(4)\text{H}_3$ and $\text{N}(1)\text{H}_3$, 3.99 (s, 3H) for $\text{N}(2)\text{H}_3$ and 3.59 (s, 3H) for $\text{N}(3)\text{H}_3$, 7.24–8.7 (m, 6H) for 8-quinolinol. Color: brown.

Diamminebis(8-quinolinolato)cobalt(III) Nitrate Monohydrate

(10). This complex was prepared from diamminebis-(8-quinolinolato)cobalt(III) chloride hydrate¹⁾ (**7**) (1.0 g, 2.30 mmol) and silver nitrate (0.39 g, 2.30 mmol) according to the method of **9**, and recrystallized from methanol-water (1 : 1) twice. Yield: 0.81 g (76.4%). Found: C, 46.92; H, 4.61; N, 15.39%. Calcd for $\text{CoC}_{18}\text{H}_{20}\text{N}_5\text{O}_6$ (M.W. 461.33) C, 46.86; H, 4.37; N, 15.18%. Dec 193—195 °C. Absorption spectrum: 300 nm ($\epsilon=3600$), 319 (3000), 337 (3100) and 408 (6100) in methanol. ¹H-NMR spectrum δ : 3.09 ppm (s, 6H) for NH_3 , 7.0—9.1 (m, 12H) for 8-quinolinol. Color: yellowish brown.

Tetraammine(8-quinolinolato)cobalt(III) Picrate (11).

An aqueous solution of **8** (0.5 g, 1.39 mmol) was added to a solution of picric acid (0.61 g, 2.65 mmol), the mixture was stirred, and the separated yellowish brown complex was filtered and recrystallized from methanol. Yield: 0.82 g (81.2%). Dec 156—159 °C. Found: C, 34.88; H, 3.09; N, 21.42%. Calcd for $\text{CoC}_{21}\text{H}_{22}\text{N}_{11}\text{O}_{15}$ (M.W. 727.41) C, 34.68; H, 3.05; N, 21.18%. Color: yellowish brown.

Diamminebis(8-quinolinolato)cobalt(III) Picrate (12). This complex was prepared from **7** (1 g, 2.30 mmol) and picric acid (0.053 g, 2.31 mmol) according to the method of **11**, and recrystallized from methanol. Yield: 1.1 g (78.6%). Dec 200—203 °C. Found: C, 47.57; H, 3.32; N, 15.97%. Calcd for $\text{CoC}_{24}\text{H}_{20}\text{N}_7\text{O}_9$ (M.W. 609.40) C, 47.30; H, 3.31; N, 16.09%. Color: yellow.

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