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The Preparation and Properties of Ethylenediamine(2-methyl-8-quinolinolato)cobalt(III) Complexes†

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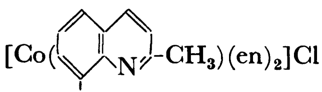
Ethylenediaminebis(2-methyl-8-quinolinolato)cobalt(III) complexes and bis(ethylenediamine)(2-methyl-8-quinolinolato)cobalt(III) complexes have been isolated and characterized by analytical and spectroscopic methods. In the former complexes, the NMR spectra indicate that the two nitrogen atoms of the coordinated 2-methyl-8-quinolinolato ligands are in the *trans* positions, whereas the two oxygen atoms are in the *cis* positions.

A few investigations of the stereochemistry of bis(8-quinolinolato)metal complexes, $[\mathrm{M(oxine)_2X_2}]$, in an octahedral configuration have been reported by some authors.[1–6] The configuration of the coordinated 8-quinolinolato ligands in their complexes is in the *trans* positions for two oxygen atoms and in the *cis* positions for two nitrogen atoms except for the dicarbonyl complex[6] which is in the *cis* positions for both the two oxygen atoms and the two nitrogen atoms. However, a complex of the configurations in the *cis* positions for two oxygen atoms and in the *trans* positions for two nitrogen atoms of the coordinated 8-quinolinolato ligands has not yet been reported.

Previously, we have been concerned with ethylenediaminebis(8-quinolinolato)cobalt(III) complexes,[7] which are in the *cis* positions for the two oxygen atoms of the coordinated 8-quinolinolato ligands. However, it has not been resolved whether the two nitrogen atoms of the coordinated 8-quinolinolato ligands are in the *trans* or the *cis* positions. An X-ray study of the complexes has not yet been made, because the crystals could not be obtained. We have found that the two methyl groups of the coordinated 2-methyl-8-quinolinolato ligands in the complexes have a steric hindrance against the amine protons of the coordinated ethylenediamine ligand. Thus, the present paper describes the preparation and properties of the ethylenediaminebis(2-methyl-8-quinolinolato)cobalt(III) complexes and bis(ethylenediamine)(2-methyl-8-quinolinolato)cobalt(III) complexes, and deals with the identification of the configuration of the former complexes.

Results and Discussion

Ethylenediaminebis(2-methyl-8-quinolinolato)cobalt(III) chloride hydrate,



$[\mathrm{Co}(\mathrm{C_9H_5(O)N\text{-}CH_3})(\mathrm{en})_2]\mathrm{Cl}\cdot$

$\mathrm{H_2O}$ (**1**) has three isomers A, B, and C as is shown in Fig. 1. The isomers of A and C have C_2 symmetry, while that of B has C_1 symmetry. In isomer A, the two methyl groups of the coordinated 2-methyl-8-quinolinolato ligands are far from both the *N*-Ha and *N*-Hb amine protons of the coordinated ethylenediamine ligand. Thus, in the ^{1}H NMR spectrum of isomer A, the amine proton signals of the coordinated ethylenediamine ligand can differ little from those of the corresponding 8-quinolinolato chloride dihydrate $[\mathrm{Co(oxine)_2en}]\mathrm{Cl}\cdot 2\mathrm{H_2O}$ (**2**), previous reported.[7] While, in the isomer C, the two methyl groups of the coordinated 2-methyl-8-quinolinolato ligands are very near both the *N*-Ha and *N*-Hb amine protons of the coordinated ethylenediamine ligand, *i.e.*, the amine proton signals of the ^{1}H NMR spectrum should be different from those of **2**. The two methyl groups in the isomer B are at different positions from those of A and C. Accordingly, the distinction between isomers A, B, or C should be evident in the NMR spectrum.

Complex **1** has been isolated by chromatographic separation from a reaction mixture of *trans*-$[\mathrm{CoCl_2en_2}]\mathrm{Cl}$,[8] $\mathrm{Ag_2O}$, and 2-methyl-8-quinolinol. The corresponding nitrate (**3**) or picrate (**4**) has been prepared from the reaction mixture of **1** and silver nitrate or picric acid, respectively. The color of **1** in the solid state is brown, **3** is dark brown and **4** is yellowish green. Complexes **1** and **3** are soluble in alcohols, DMSO, $\mathrm{CF_3COOH}$ and water, though complex **4** is soluble in DMSO, and somewhat soluble in acetone and methanol.

^{1}H NMR and ^{13}C NMR spectra of **1** are suggestive of the present of C_2 symmetry[5,9] from Figs. 2 and 3, *i.e.*, the isomer of **1** can be suggested to be either A or C. In the ^{1}H NMR spectrum of **1**, the signals at 6.9—8.2 ppm (10H) are assigned to the protons of the coordinated 2-methyl-8-quinolinolato ligand. The signals (10H) at 2.55 ppm and 2.54—2.70 ppm are assigned to the methyl and methylene protons of the coordinated ligands. The amine protons of the coordinated ethylenediamine ligand showed two singlet signals at 4.88 ppm (2H) and 5.87 ppm (2H). A clear distinction of **1** and **2** was found in the amine proton signals of their ^{1}H NMR spectra as is shown in Fig. 2. The amine proton signals at 4.88 and 5.87 ppm of **1** shift to 5.27 and 5.79 ppm of **2**, respectively in the same conditions ($6.2\pm0.05\times10^{-2}$ mol dm^{-3} DMSO-d_6 solution). Also, this behavior occurs in 50% ($\mathrm{CF_3COOH}+\mathrm{D_2O}$) solution as is shown in Table 1. The shift of signal at 4.88 ppm is larger than that of 5.87 ppm. This behavior can be based on the steric effect of the methyl groups upon the amine protons. Then, the signal at 4.88 ppm is assigned to the *N*-Ha amine protons, because they are near both methyl groups. The signal at 5.87 ppm is assigned to *N*-Hb amine protons. Thus, complex **1** has been assigned to isomer C, which has been in the *trans* position for the two nitrogen atoms and in the *cis* position for the two oxygen atoms

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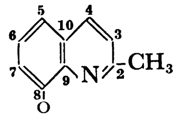
[†] Part III: Cobalt(III) Complexes with $[\mathrm{N}_{6-n}\mathrm{X}_n]$ Type Ligand. Part I: Ref. 5; Part II: Ref. 7.

TABLE 1. SOME PHYSICAL PROPERTIES OF COMPLEXES **1—8**

^{1}H No.	$NH_2CH_2CH_2NH_2$ δ			2-Methyl-8-quinolinolato δ		Picrate δ	Absorption bands in methanol λ/nm (ε)			Electro conductivity of aqueous solutions
	[CH_2] CH_2+CH_3	[NH_2] Ha	Hb	8-Quinolinolato	CH_3					S cm^2 equiv.$^{-1}$
1	2.54—2.70 (10H)	4.88 (2H)	5.87 (2H)	6.9—8.2 (10H)	2.55$^{1)}$		326 (1980)	342 (2240)	398 (5220)	125
	[3.06(4H)]	3.99 (2H)	5.22 (2H)	7.1—8.2 (10H)	2.47 (6H)$^{2)}$					
2	[2.75(4H)]	5.27 (2H)	5.79 (2H)	6.9—8.4 (12H)$^{1)}$	—		325 (2400)	339 (2960)	404 (5730)	130
	[3.27(4H)]	4.62 (2H)	5.21 (2H)	7.1—8.3 (12H)$^{2)}$	—					
3	2.50—2.75 (10H)	4.87 (2H)	5.83 (2H)	6.8—8.2 (10H)	2.55$^{1)}$		326 (2080)	341 (2360)	398 (5420)	
4	2.54—2.84 (10H)	4.91 (2H)	5.87 (2H)	6.8—8.2 (10H)	2.57	8.51 (2H)$^{1)}$		362 (19530)	393 (18370)	
5	2.59—3.18 (11H)	[4.19—5.92 (8H)]		7.1—8.4 (5H)	2.94$^{3)}$		320 (985)	341 (975)	398 (2690)	230
6	2.55—3.12 (11H)	[4.03—5.80 (8H)]		7.0—8.3 (5H)	2.91$^{3)}$		320 (1090)	341 (1070)	398 (2900)	
7	2.55—2.90 (11H)	[4.00—6.06 (8H)]		6.8—8.2 (5H)	2.78	8.49 (4H)$^{1)}$		357 (22300)	390 (17620)	
8*	2.92(8H)	[4.12—5.34 (8H)]		7.0—8.7 (6H)$^{3)}$	—		324 (1150)	338 (1250)	407 (2900)	270



^{13}C	$NH_2CH_2CH_2NH_2$ δ	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	CH_3
1	45.5	164.8	114.6	139.6	127.3	117.3	129.7	145.9	165.6	129.0	22.2$^{4)}$
5	43.9 44.6 45.7 46.7	164.4	115.1	140.9	127.3	116.4	129.8	145.7	164.8	129.8	24.0$^{4)}$

Solvents and Standard: 1) DMSO-d_6, internal TMS; 2) 50% ($CF_3COOH+D_2O$), internal DSS; 3) 1.8 mol dm^{-3} D_2SO_4, internal DSS; 4) D_2O, internal dioxane (δ=67.4). *: Ref. 7.

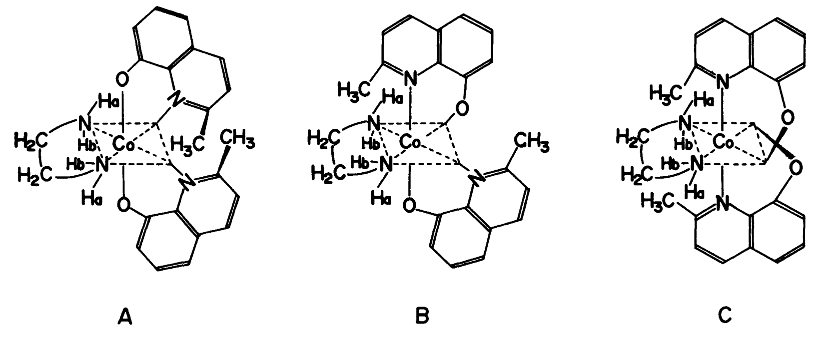
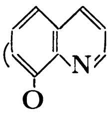


Fig. 1. The isomers of [Co(2-Me-oxine)$_2$en]Cl·H_2O.

of the coordinated 2-methyl-8-quinolinolato ligands. In the ^{13}C NMR spectrum of **1** as is shown in Fig. 3, the chemical shifts of the coordinated 2-methyl-8-quinolinolato ligands were assigned on the basis of the results of the complex **2**;[7] they are collected in Table 1.

Bis(ethylenediamine)(2-methyl-8-quinolinolato)cobalt(III) chloride dihydrate, [Co( -CH_3)(en)$_2$]Cl·$2H_2O$ (**5**) has been isolated from a reaction mixture of *trans*-[$CoCl_2en_2$]Cl, Ag_2O, and 2-methyl-8-quinolinol. The corresponding nitrate (**6**) or picrate (**7**) has been prepared from the reaction mixture of **5** and silver nitrate or picric acid, respectively. The color of **5** in the solid state is russet brown, **6** is brown, and **7** is yellowish brown. Complexes **5** and **6** are soluble in DMSO, methanol and water, and they are somewhat soluble in ethanol, though complex **7** is soluble in acetone and DMSO and somewhat soluble in methanol. The signals of the methyl, metyhlene, and 8-quinolinolato

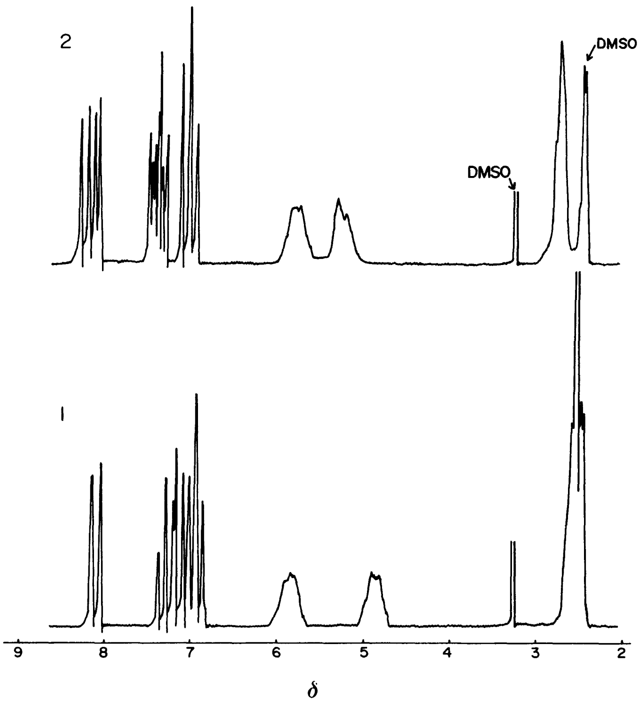


Fig. 2. The ^1H NMR spectra of $[Co(2\text{-}Me\text{-}oxine)_2en]Cl\cdot H_2O$ (**1**) and $[Co(oxine)_2en]Cl\cdot 2H_2O$ (**2**) in DMSO-d_6.

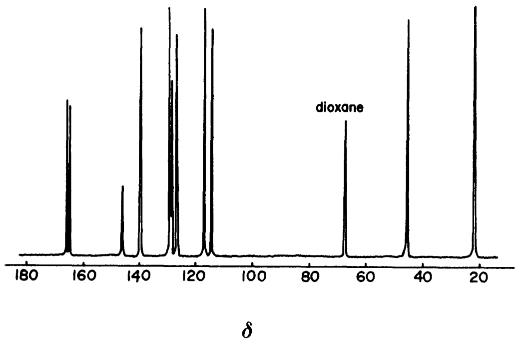


Fig. 3. The ^{13}C NMR spectrum of $[Co(2\text{-}Me\text{-}oxine)_2en]Cl\cdot H_2O$ in D_2O.

protons and carbons and of amine protons of the coordinated ligands in **5**—**7** were assigned on the basis of the results of the bis(ethylenediamine)(8-quinolinolato)cobalt(III) chloride dihydrate, $[Co(oxine)en_2]Cl\cdot 2H_2O$ (**8**), in the previous paper,[7] and collected in Table 1.

Absorption spectra of **1**—**3**, **5**, **6**, and **8** show three absorption bands at around 325, 340, and 400 nm in methanol as is shown in Table 1. The absorption bands at 340 nm of **1**—**3** complexes are stronger than those at 325 nm, though those at 325 nm of **5** and **6** are stronger than those at 340 nm. The ε's of three bands of **1** or **3** and **5** or **6** are smaller than those of **2** and **8**, respectively because it can be based on the inductive effect of the methly group of the chelate ligand. The absorption bands at around 400 nm are charge transfer band.[5] All complexes are diamagnetic. Their electric conductivities in an aqueous solution were collected in Table 1.

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 electric conductivities of an aqueous solution were determined by the use of a conductometric meter CM-30 (Shimadzu) at room temperature. The magnetic susceptibilities were measured by Faraday's method using a magnetic balance (Shimadzu) at room temperature.

Preparation of Complexes. Ethylenediaminebis(2-methyl-8-quinolinolato)cobalt(III) Chloride Hydrate (1) and Bis(ethylenediamine)(2-methyl-8-quinolinolato)cobalt(III) Chloride Dihydrate (5): To 100 cm³ of an aqueous solution of $[CoCl(OH)en_2]^+$ which was prepared from *trans*-$[CoCl_2en_2]Cl$ (10.0 g, 35.0 mmol) and Ag_2O (4.05 g, 17.5 mmol), a methanol solution (120 cm³) of 2-methyl-8-quinolinol (5.5 g, 34.5 mmol) was added dropwise. The liquid was stirred for 45 h at 60 °C. The reaction mixtures were concentrated on a rotary evaporator and dried over silica gel. Complexes **1** and **5** were extracted with methanol from the dried mixture. The methanol extract was concentrated, and the solution was chromatography on a column of alumina. On elution with ethanol, the first band (complex **1**) was collected and the solution concentrated. The precipitated complex was recrystallized from ethanol–ether twice. The second band (complex **5**) was eluted with methanol and the solution was concentrated. This complex was recrystllized from methanol–ethanol (1:2) twice. Yields: 7.72 g (45.1%) for **1**, 0.62 g (4.0%) for **5**. Found **1**: C, 54.59; H, 5.27; N, 11.05; Cl, 7.76%. **5**: C, 37.80; H, 6.39; N, 16.06; Cl, 16.40%. Calcd for **1**: $CoC_{22}H_{26}N_4O_3Cl$ (MW 488.86) C, 54.05; H, 5.36; N, 11.46; Cl, 7.25%. **5**: $CoC_{14}H_{28}N_5O_3Cl_2$ (MW 444.25) C, 37.85; H, 6.35; N, 15.76; Cl, 15.96%.

Ethylenediaminebis(2-methyl-8-quinolinolato)cobalt(III) Nitrate (3): To an aqueous solution of **1** (0.5 g, 1.0 mmol) was added an aqueous solution silver nitrate (0.17 g, 1.0 mmol). The mixture was stirred, and the silver chloride precipitated was filtered. The filtrate was concentrated on a rotary evaporator. A small amount of silver complex in the filtrate was removed by column chromatographyon alumina. The elution band of methanol was collected and the solution was concentrated. Complex **3**, thus precipitated, was recrystallized from ethanol–ether twice. Yield: 0.35 g (70.4%). Found: C, 52.69; H, 5.15; N, 14.12%. Calcd for $CoC_{22}H_{24}N_5O_5$ (MW 497.40) C, 53.12; H, 4.86; N, 14.08%.

Ethylenediaminebis(2-methyl-8-quinolinolato)cobalt(III) Picrate (4): An aqueous solution of **1** (0.5 g, 1.0 mmol) was added to a solution of picric acid (0.23 g, 1.0 mmol); the mixture was stirred, and the separated yellowish green complex was filtered and recrystallized from methanol. Yield: 0.60 g (90.4%). Found: C, 50.01; H, 3.99; N, 15.25%. Calcd for $CoC_{28}H_{26}N_7O_9$ (MW 663.50) C, 50.69; H, 3.95; N, 14.78%.

Bis(ethylenediamine)(2-methyl-8-quinolinolato)cobalt(III) Nitrate Hydrate (6): This complex was prepared from the reaction mixture of **5** (0.5 g, 1.1 mmol) and silver nitrate (0.38 g, 2.2 mmol) by the method of complex **3**, and recrystallized from water–ethanol twice. Yield: 0.31 g (58.8%). Found: C, 34.90; H, 5.58; N, 20.64%. Calcd for $CoC_{14}H_{26}N_7O_8$ (MW 479.35) C, 35.08; H, 5.47; N, 20.45%.

Bis(ethylenediamine)(2-methyl-8-quinolinolato)cobalt(III) Picrate (7): An aqueous solution of **5** (0.5 g, 1.1 mmol) was added to a solution of picric acid (0.51 g, 2.2 mmol), the mixture was stirred, and the separated russet brown complex was filtered and recrystallized from methanol. Yield: 0.59 g (67.6%). Found: C, 39.54; H, 4.17; N, 19.14%. Calcd for $CoC_{26}H_{28}N_{11}O_{15}$ (MW 793.52) C, 39.35; H, 3.56; N, 19.42%.

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