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ISOLATION OF AMMINE(8-QUINOLINOLATO)COBALT(III) CHLORIDE

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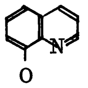
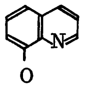
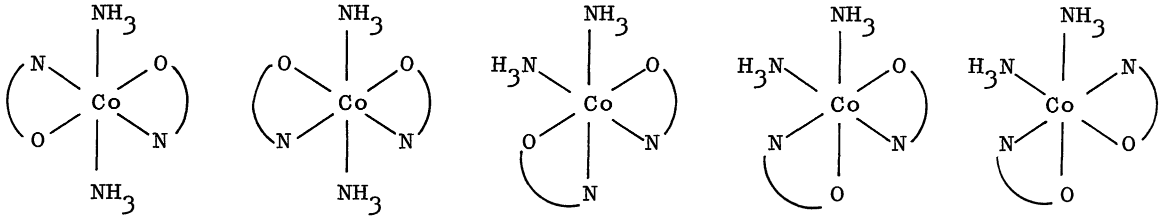
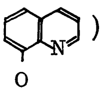
Tetraammine(8-quinolinolato)cobalt(III) chloride hydrate and diamminebis(8-quinolinolato)cobalt(III) chloride hydrate have been isolated and characterized by analytical and spectroscopic methods.

Although the preparation of tris(8-quinolinolato)metal complexes[1)] and alkyl-,[2)] and dichlorobis(8-quinolinolato)metal complexes[3)] has already been reported by many researchers, the preparation of ammine(8-quinolinolato)-metal complexes has never been described. We have now isolated tetraammine-(8-quinolinolato)cobalt(III) chloride hydrate, $[Co($  $)(NH_3)_4]Cl_2\cdot H_2O$ (**1**), and diamminebis(8-quinolinolato)cobalt(III) chloride hydrate, $[Co($  $)_2(NH_3)_2]Cl\cdot H_2O$ (**2**). These complexes were prepared as follows: a 28% ammonia solution (40 ml) was added to an aqueous solution (5 ml) of $CoCl_2\cdot 6H_2O$ (5.0 g, 21.0 mmol), and about 3ml of a 30% H_2O_2 solution was added slowly to the solution at 0 °C. The color of the solution changed to red from brown. A methanol solution (50 ml) of 8-quinolinol (2,0 g, 14.0 mmol) was added dropwise to the solution for 90 minutes at 60 °C. The solution was refluxed for 1 day. The yellowish green tris(8-quinolinolato)-cobalt(III) complex (**3**) precipitated was filtered and the filtrate was concentrated with a rotary evaporator at 50 °C and dried over silicagel. Complexes **1** and **2** were extracted with methanol from the dried reaction mixture. The separation of **1** and **2** from the methanol solution was tried by chromatography on alumina. On elution with methanol, the band of product splits into three. The first eluate (Complex **2**) was concentrated and **2** was recrystallized from methanol-water (1:1) two times. Then, the eluent was switched to water, and a mixture of the second and third bands was collected, concentrated and dried over silicagel. Complex **1** was extracted with dry methanol from the dried mixture. Complex **1** was soluble in water and precipitated by addition of acetone. Hexaamminecobalt(III) chloride (**4**) was not extracted by dry methanol from the dried mixture. Yield **1**: 1.10 g (14.6%), **2**: 3.81 g (41.7%), **3**: 0.97 g (9.4%), and **4**: 1.02 g (20.8%). Analysis; Found **1**: C, 30.28; H, 5.58; N, 19.90; Cl, 19.79%. Calcd for $CoC_9H_{20}N_5O_2Cl_2$ (MW 360.13) C, 30.02; H, 5.60; N, 19.45; Cl, 19.69%. Found **2**: C, 49.72; H, 4.87; N, 12.65; NH_3, 7.23; Cl, 8.47%. Calcd for $CoC_{18}H_{20}N_4O_3Cl$ (MW 434.77) C, 49.73; H, 4.64; N, 12.89; NH_3, 7.83; Cl, 8.15%. Found **3**: C, 65.13; H, 3.98; N, 8.55%. Calcd for $CoC_{27}H_{18}N_3O_3$ (MW 491.39) C, 66.00; H, 3.69; N, 8.55%. M.p., **1**: 175-177 (dec), **2**: 203-205 °C. The color of **1** is brown and that of **2** is yellow. The by-products (**3** and **4**) are produced in greater amounts at a reaction temperature below 55 °C. Complex **1** is very soluble in water, and soluble in both methanol and dimethylsulfoxide. Complex **2** is soluble in both methanol and dimethylsulfoxide, and slightly soluble in water. These complexes are insoluble in most other common organic solvents. Although the geometrical structures,



2a **2b** **2c** **2d** **2e**

Fig. 1. Trans- and cis- isomers of the [Co( $)_2(NH_3)_2]Cl\cdot H_2O$

2a~**2e**, are possible for the diamminebis(8-quinolinolato)complex, complex **2** obtained is considered to be a pure isomer from the NMR spectrum and behavior in chromatography with Dowex 50W-X2, X8 and X12.[4] Electric coductivities of **1** and **2** in aqueous solutions were 265 S cm^2 eq^{-1} and 140 S cm^2 eq^{-1}, respectively. The complexes are diamagnetic and should be cobalt(III) complexes of the low spin type.

The ^{1}H-NMR spectra of **1** and **2** were measured in 1.8 mol D_2SO_4 or DMSO-d_6 solutions. The multiplet signals (6H for **1** and 12H for **2**) in the region of 7.0-9.2 ppm are assigned to the protons of the coordinated 8-quinolinolato ligand of both complexes as shown in Fig. 2. The protons of the coordinated NH_3 ligands of **1** showed three singlet signals in the intensity ratio of 2:1:1. The signal (3.37 ppm, 6H) at the highest field is assigned to the protons of the two ammine ligands of $N(1)H_3$ and $N(4)H_3$ in a position cis to the coordinated 8-quinolinolato ligand, because the two ammine ligands are considered to be equivalent. The two singlets at 3.64 (3H) and at 4.02 (3H) ppm are assigned to the protons of the two ammine ligands of $N(3)H_3$ and $N(2)H_3$ in a position trans to the oxygen and the nitrogen of the chelate ligand, respectively.$^{5-6)}$ In the spectrum of 2, the singlet

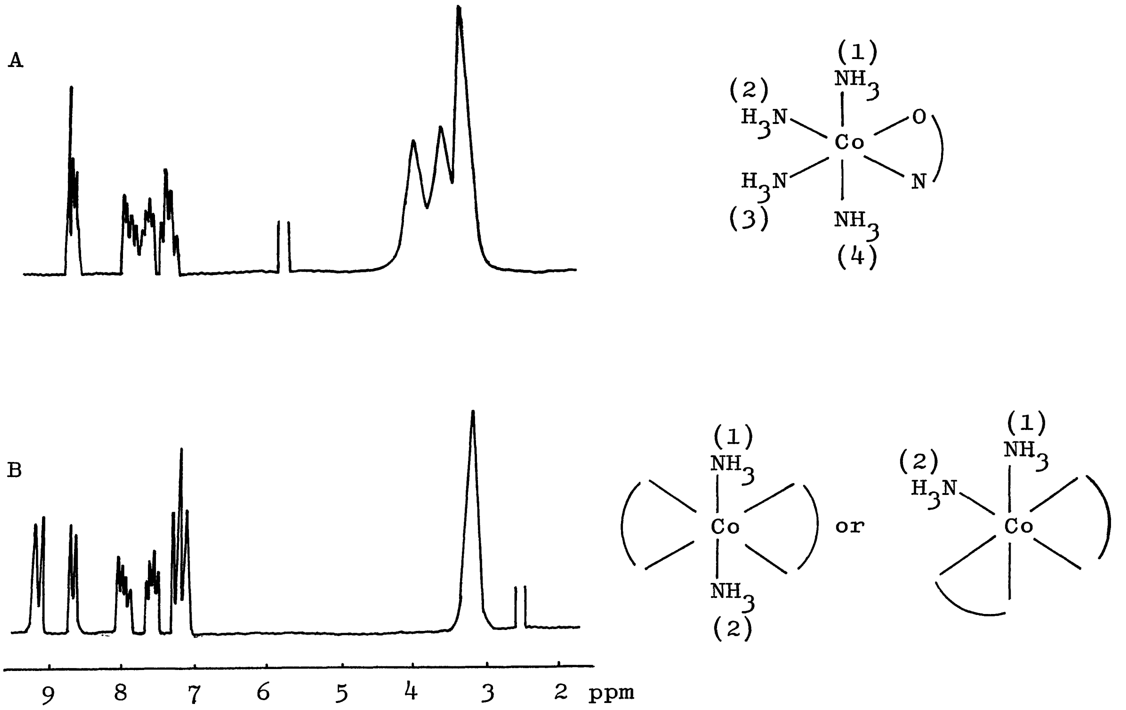


Fig. 2. ^{1}H-NMR spectra of Ammine(8-quinolinolato)cobalt(III) chloride

A: $[Co(C_9H_6NO)(NH_3)_4]Cl_2 \cdot H_2O$, B: $[Co(C_9H_6NO)_2(NH_3)_2]Cl \cdot H_2O$

signal (6H) at 3.12 ppm is assigned to the protons of the two ammine ligands of $N(1)H_3$ and $N(2)H_3$ in a position trans or cis to the nitrogen and the oxygen of the coordinated 8-quinolinolato ligands. The structure of **2** can not be uniguely defined from the ^{1}H-NMR spectrum. However, the X-ray analyses7-9) by many researchers have shown that the two oxygen atoms of the coordinated 8-quinolinolato ligands in an octahedral configuration are in trans positions whereas the two nitrogen atoms are in cis positions such as in **2c**. Thus it seems that the structure of **2** is **2c**. This is consistent with the presence of C_2 symmetry as suggested by NMR spectra.

The absorption spectrum of **1** in methanol has three absorption bands at 325 nm (ε=1020), 338 (1230) and 401 (2510), while that of **2** in methanol has three absorption bands at 321 nm (ε=2970), 337 (3190) and 407 (6300). The absorption band at 312 nm of 8-quinolinol is shifted to 400-407 nm upon formation of the complexes.10) The bands around 400-407 nm are considered to be charge-transfer band.

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