Cobalt(III) Complexes with Quadridentate Ligands. XI.[1) The Preparation and Properties of *cis*-α-Isomer of the Salicylato(triethylenetetramine)cobalt(III) Complex

Yoshihisa YAMAMOTO,* Eiko TOYOTA, Toyo KUMON, and Haruo SEKIZAKI
Faculty of Pharmaceutical Sciences, Higashi Nippon Gakuen University,
Ishikari-Tobetsu, Hokkaido 061-02

(Received June 10, 1991)

Synopsis. *cis*-α-Salicylato(triethylenetetramine)cobalt(III) chloride, *cis*-α-[Co(sal)trien]Cl, has been isolated and characterized by means of both analytical and spectroscopic methods.

In this series we have described the preparation and properties of isomers of salicylato-,2) thiosalicylato-,3) salicylaldehydato-,1,4) or 8-quinolinolato(triethylenetetramine)cobalt(III) complexes.5) The *cis*-β_1 and β_2-isomers of the complexes have been obtained from a reaction mixture of *cis*-α-[$CoCl_2$trien]Cl, Ag_2O, and organic compounds.1–5) However, the *cis*-α-isomer of the complexes has not yet been obtained, because the treatment of the *cis*-α-[$CoCl_2$trien]Cl in neutral or alkaline aqueous solutions results in quantitative isomerization to the *cis*-β-triethylenetetramine configuration.2,6)

Now, we have isolated *cis*-α-salicylato(triethylenetetramine)cobalt(III) chloride, *cis*-α-[Co(sal)trien]Cl, in methanol by a direct preparation method. The present paper deals with the preparation and properties of *cis*-α-[Co(sal)trien]Cl.

Experimental

Measurements. The electric conductivity was determined by the use of a CM-40S conductivity meter (TOA) in an aqueous solution at room temperature. The IR spectrum was recorded in KBr disks with a 270-30 spectrophotometer (Hitachi). The visible absorption spectrum was recorded in water with a Shimadzu UV-210 recording spectrophotometer. The ^1H and ^{13}C NMR spectra were recorded with a JNM-FX90Q FT NMR spectrometer (JEOL). The melting point was measured on an MP-500D apparatus (Yanako).

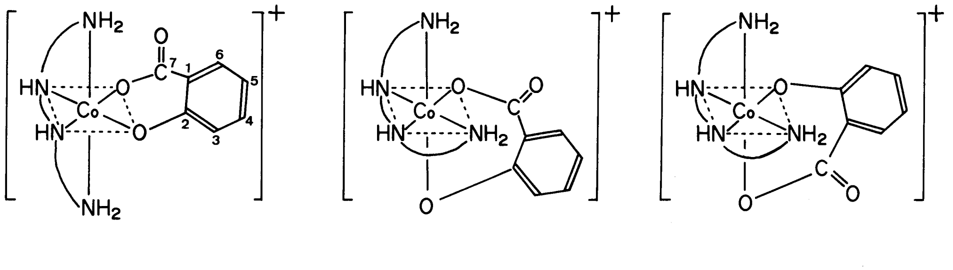
Preparation of Complexes. *cis*-α-Salicylato(triethylenetetramine)cobalt(III) Chloride (1) and the Corresponding *cis*-β_1- (2) and β_2-Isomers2) (3): A methanol solution (60 cm^3) of triethylenetetramine (7.31 g, 50.0 mmol) and sodium salicylate (8.0 g, 50.0 mmol) were added to a methanol solution (30 cm^3) of $CoCl_2\cdot 6H_2O$ (11.9 g, 50.0 mmol). Air was bubbled into the solution for 5 h, and the reaction mixture was stirred at 50 °C for 7 h. It was then concentrated on a rotary evaporator. The precipitated russet complex (*cis*-β_2-isomer) was filtered (3.55 g), and the filtrate was concentrated. Then, the separated NaCl was removed, and the filtrate was concentrated. The isolation of complex **1** in the filtrate was achieved by column chromatography on alumina. Upon elution with MeOH–EtOH (1:1), the effluent of the first russet band was collected, concentrated, and dried. The dried product (mixture of *cis*-α and β_2-isomers) of 4.02 g was dissolved in 60 cm^3 of hot methanol, and cooled in an icebox. The precipitated russet complex, *cis*-α-[Co(sal)trien]Cl (**1**), was filtered and recrystallized from methanol. Yield: 2.56 g (13.6%). Found: C, 41.28; H, 5.77; N, 14.61; Cl, 9.64%. Calcd for $CoC_{13}H_{22}N_4O_3Cl$ (MW 376.73): C, 41.44; H, 5.89; N, 14.88; Cl, 9.41%. $\Lambda=91$ S cm^2 mol^{-1} in water. Mp 234—235 °C. IR 1040, 1065 cm^{-1} (NH_2 twisting). Absorption spectrum (H_2O): 330 nm ($\epsilon=2900$), 513 (205). ^1H NMR (1.8 mol dm^{-3} D_2SO_4) $\delta=2.4$—3.7 (12H, CH_2); 5.00 (1H, NH_2), 5.27 (3H, NH_2); 5.99 (1H, NH), 6.31 (1H, NH); 6.6—7.9 (4H, salicylato). ^{13}C NMR (D_2O) $\delta=42.8$ (NH_2- side CH_2), 53.9, 54.7, 55.8, 56.0 (NH- side CH_2); $\delta=117.2$ (C-3), 117.9 (C-1), 124.1 (C-5), 132.7 (C-6), 134.6 (C-4), 167.6 (C-2), 174.2 (C-7).

Complexes **2** and **3** were obtained from a reaction mixture of an aqueous solution (100 cm^3) of trien (7.31 g, 50.0 mmol), sodium salicylate (8.0 g, 50.0 mmol), and $CoCl_2\cdot 6H_2O$ (11.9 g, 50.0 mmol) according to the preparation method of **1**; complex **1**, however, could not be obtained from the reaction mixture. Yields: 0.9 g (4.6%) for **2**, 6.53 g (33.1%) for **3**.

Results and Discussion

The octahedral salicylato(triethylenetetramine)cobalt(III) complex exists in three isomeric forms: *cis*-α, *cis*-β_1, and *cis*-β_2, as shown in Fig. 1.

cis-α-Salicylato(triethylenetetramine)cobalt(III) chloride, *cis*-α-[Co(sal)trien]Cl (**1**), has been obtained from a reaction mixture of $CoCl_2\cdot 6H_2O$, trien, and sodium salicylate by air oxidation in methanol at



cis-α cis-β_1 cis-β_2

Fig. 1. The *cis*-α, β_1, and β_2 configurations of salicylato(triethylenetetramine)cobalt(III) complex.

pH=7.6. Although *cis*-β_1-[Co(sal)trien]Cl·H_2O (**2**) and *cis*-β_2-[Co(sal)trien]Cl·H_2O (**3**) were obtained from a reaction mixture of $CoCl_2 \cdot 6H_2O$, trien, and sodium salicylate by air oxidation in an aqueous solution, complex **1** could not be obtained from the reaction mixture. Thus, the *cis*-α-isomer is formed in methanol.

The color of **1** is russet. The melting point of **1** is 234—235 °C. The electric conductivity of **1** in an aqueous solution is 91 S cm^2 mol^{-1}. Complex **1** is very soluble in water and dimethyl sulfoxide, and soluble in alcohols, but insoluble in other common organic solvents.

The absorption spectrum of **1** was measured in water. The absorption bands at 330 and 513 nm were assigned to the absorption of salicylato and the first d-d absorption bands, respectively. The ^{13}C NMR spectrum of **1** was measured in D_2O (Fig. 2). Seven signals at δ=117—175 were assigned to the carbons of the coordinated salicylato ligand by a comparison with those[2)] of **2** and **3**. The signals at δ=42.8 and at δ=53—56 were assigned to the NH_2- and NH- side methylene carbons,[7)] respectively. The ^1H NMR spectrum of **1** was measured in 1.8 mol dm^{-3} D_2SO_4 (Fig. 2). The signals at δ=2.4—3.7 (12H), δ=4.7—5.5 (4H), and δ=5.8—6.5 (2H) were assigned to the methylene, primary amine, and secondary amine protons of the coordinated trien ligand, respectively, by comparisons with those[2)] of **2** and **3**. The lowest field signals at δ=6.6—7.9 (4H) were assigned to the coordinated salicylato protons.

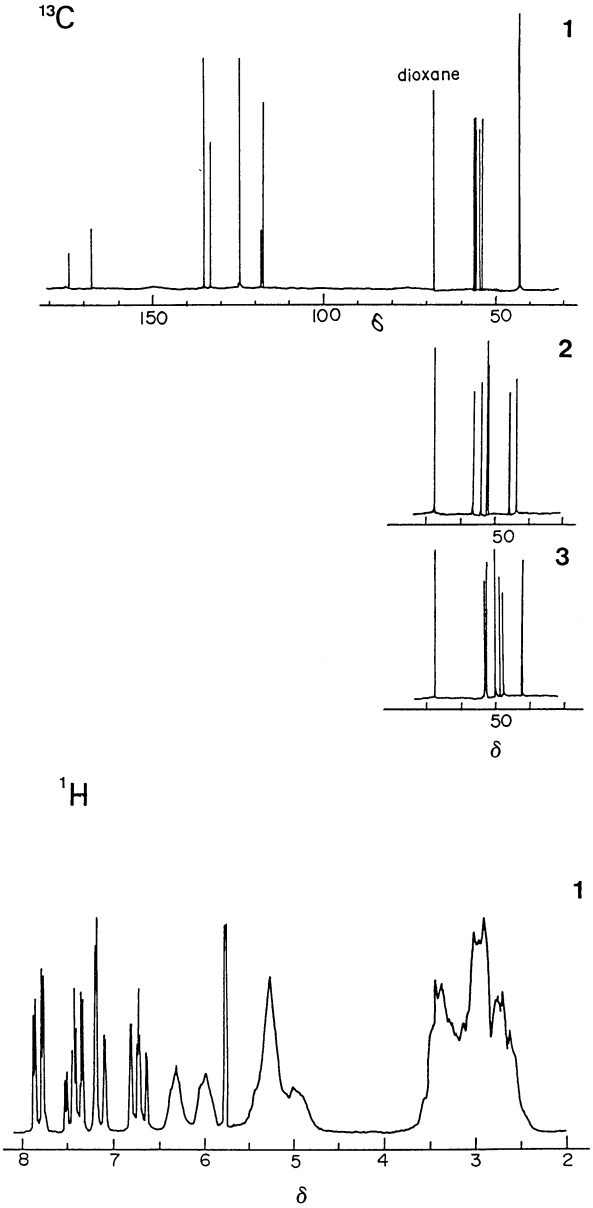


Fig. 2. The ^1H and ^{13}C NMR spectra of complexes **1**—**3**. **1**: *cis*-α-[Co(sal)trien]Cl, **2**: *cis*-β_1-[Co(sal)trien]Cl·H_2O, **3**: *cis*-β_2-[Co(sal)trien]Cl·H_2O. Solvent and standard. ^1H: 1.8 mol dm^{-3} D_2SO_4, internal DSS. ^{13}C: D_2O, internal dioxane (δ=67.4).

The IR spectrum of **1** showed two strong absorptions at 1040 and 1065 cm^{-1} in the NH_2 twisting region (990—1100 cm^{-1}), whereas those[2)] of **2** and **3** showed four signals. This suggests that complex **1** can be assigned to the *cis*-α-triethylenetetramine configuration.[8)] In the ^{13}C NMR spectrum (Fig. 2), the signal of two NH_2- side methylene carbons overlapps, and the difference

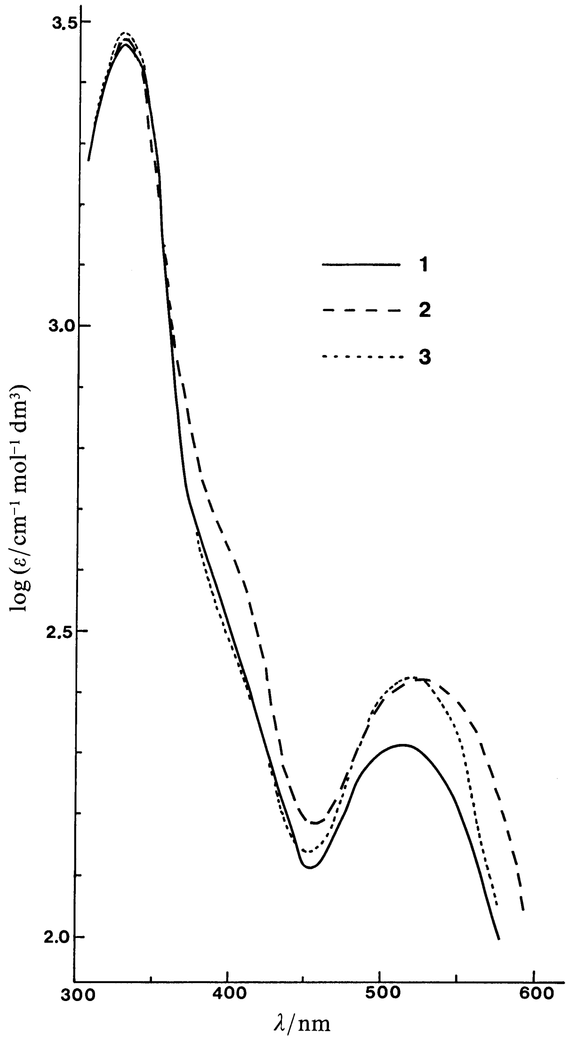


Fig. 3. The absorption spectra of complexes **1**—**3** in water. **1**: *cis*-α-[Co(sal)trien]Cl, **2**: *cis*-β_1-[Co(sal)trien]Cl·H_2O, **3**: *cis*-β_2-[Co(sal)trien]Cl·H_2O.

($\Delta\delta$=2.1) of the chemical shifts of the NH- side methylene carbons of **1** is smaller than that²⁾ ($\Delta\delta$=4.7±0.3) of **2** and **3**, i.e., the spectrum of **1** is symmetric in contrast to those of **2** and **3**. In the ^{1}H NMR spectrum, the chemical shifts (δ=4.7—5.5) of the proton signal of the NH_2 group of the coordinated trien ligand of **1** are at a lower field than those²⁾ (δ=4.0—5.4) of **2** and **3**, i.e., the NH_2 group is considered to be at a position cis to the carboxyl or phenoxyl oxygen of the coordinated salicylato ligand, which is more electronegative²,⁹⁾ than the nitrogen of the NH_2 group of coordinated trien ligand. The chemical shifts (δ=5.99 and 6.30) of the proton signals of the NH group are at a higher field than those²⁾ (δ=6.1—6.7) of **2** and **3**, i.e., the NH group of **1** is considered to be at a position trans to the carboxyl or phenoxyl oxygen of the salicylato ligand. The spectral patterns of the methylene and amine proton signals of the trien ligand of **1** are very close to those of *cis*-α-[Co(gly)trien]$^{2+}$, which was examined by X-ray diffraction.¹⁰⁾ Thus, complex **1** has been assigned to *cis*-α-[Co(sal)trien]Cl.

The different properties of between complex **1** and complexes **2** and **3** are as follows: i) complex **1** could not be obtained from a reaction mixture of an aqueous solution, but complexes **2** and **3** could be obtained from the reaction mixture. Complex **1** could not isomerize to **2** and **3** in neutral or alkaline aqueous solution and alcohols, but complex **2** isomerizes to **3**. ii) the first absorption band in the absorption spectrum of **1** differs remarkably from those²⁾ of **2** and **3**, i.e., the ϵ value (205) of **1** is smaller than those (270) of **2** and **3**, and the band (513 nm) of **1** appears at a shorter wavelength than those (520—530 nm) of **2** and **3** (Fig. 3).

References

1) Part X: E. Toyota and Y. Yamamoto, *Bull. Chem. Soc. Jpn.,* **62**, 3817 (1989).

2) Y. Yamamoto and E. Toyota, *Bull. Chem. Soc. Jpn.,* **52**, 2540 (1979).

3) Y. Yamamoto, K. Yoshii, E. Toyota, and K. Konno, *Bull. Chem. Soc. Jpn.,* **62**, 724 (1989).

4) Y. Yamamoto, E. Toyota, and S. Tsukuda, *Bull. Chem. Soc. Jpn.,* **58**, 1595 (1985).

5) Y. Yamamoto, E. Toyota, and Y. Yamamoto, *Bull. Chem. Soc. Jpn.,* **56**, 2721 (1983).

6) E. Kyuno, L. J. Boucher, and J. C. Bailar, Jr., *J. Am. Chem. Soc.,* **87**, 4458 (1965).

7) Y. Yamamoto, H. Kudo, and E. Toyota, *Bull. Chem. Soc. Jpn.,* **56**, 1051 (1983).

8) D. A. Buckingham and D. Jones, *Inorg. Chem.,* **4**, 1387 (1965).

9) Y. Yamamoto, *Bull. Chem. Soc. Jpn.,* **51**, 2897 (1978).

10) B. F. Anderson, J. D. Bell, D. A. Buckingham, P. J. Cresswell, G. J. Gainsford, L. G. Marzilli, G. B. Robertson, and A. M. Sargeson, *Inorg. Chem.,* **16**, 3233 (1977).