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Cobalt(III) Complexes with Quadridentate Ligands. VI.[1] The Preparation and Properties of "*cis*-β_1 and β_2"-Isomers of the Salicylaldehydato(triethylenetetramine)-cobalt(III) Complex

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Synopsis *cis*-β_1 and β_2-Salicylaldehydato(triethylenetetramine)cobalt(III) chloride dihydrate have been isolated from a reaction mixture of salicylaldehyde, *cis*-α or β-dichloro(triethylenetetramine)cobalt(III) chloride and Ag_2O. The IR spectra of the complexes showed four strong absorption peaks in the 990—1100 cm^{-1} region. The complexes were assigned to the β-form. Their *cis*-β_1 and *cis*-β_2 configurations have been established by their ^{1}H NMR spectra.

Previously, we have been concerned with the preparation and properties of isomers of the mixed-ligand complexes of *cis*-β_1, β_2-salicylato(quadridentate amine)cobalt(III) chloride hydrates,[2,3] [Co(sal)L]Cl·nH$_2$O (L: 2,2,2-tet; 2,3,2-tet; 3,2,3-tet; 3,3,3-tet. The abbreviation, tet, means tetramin; *e.g.*, triethylenetetramine is abbreviated to 2,2,2-tet). The preparation of the mixed-ligand metal complexes with salicylaldehydato and amine ligands had been very difficult, because the metal complexes with Schiff base ligands[4] had been obtained, such as (N,N'-disalicylidene-substituted triethylenetetramine)metal complexes in an octahedral configuration and (N,N'-disalicylidene-polymethylenediamine)metal complexes in a planar configuration. Thus, very little was known regarding the preparation and properties of aldehydato metal complexes with amine ligands in contrast with the large amount of information regarding salicylato metal complexes[1—3,5] with amine ligands. The present paper deals with the preparation and properties of the mixed-ligand cobalt(III) complexes with salicylaldehydato and triethylenetetramine ligands and deals with the assignments of the configuration of *cis*-β_1 and β_2 isomers.

Results and Discussion

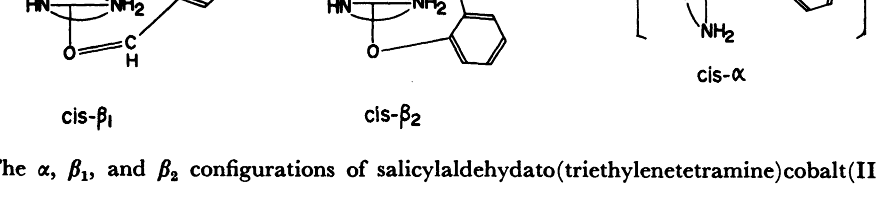
A mixture of *cis*-β_1 and β_2-salicylaldehydato(triethylenetetramine)cobalt(III) chloride dihydrate has been isolated from a reaction mixture of *cis*-α or β-[CoCl$_2$trien]Cl, Ag_2O, and salicylaldehyde. The separation of the *cis*-β_1 isomer (complex **1**) and the *cis*-β_2 isomer (complex **2**, Fig. 1) was attempted using an ion-exchange resin. The *cis*-α isomer could not be obtained.

The electric conductivities of **1** and **2** in aqueous solutions were about 210 S cm^2 equiv^{-1}. The IR spectra of **1** and **2** showed four strong peaks in the 990—1100 cm^{-1} region (*cf.* Experimental section) and five peaks in the 3000—3300 cm^{-1} region. Thus, complexes **1** and **2** were assigned to the *cis*-β configuration.[6] The electronic absorption spectrum of **1** is very similar to that of **2**. The absorption bands at 420 and 510 nm were assigned to the charge-transfer band and the first d-d absorption band ($^1T_{1g}\leftarrow{}^1A_{1g}$), respectively. In the ^{1}H NMR spectra, the lowest field signals at δ 8.5—8.6 were assigned to the aldehyde group protons,[7] and the signals at δ 2.3—3.6 and 4.3—6.7 were assigned to the methylene protons[2] and the amine protons[2] of the coordinated triethylenetetramine ligand (abbreviation: trien ligand), respectively. The methylene proton signals at δ 2.4—2.8 and 2.8—3.6 of **2** were assigned to the NH$_2$-side and NH-side methylene protons,[3] respectively. The color, solubility, IR, ^{13}C and electronic absorption spectra of **1** were similar to those of **2**.

A clear distinction between **1** and **2** complexes was found in the ^{1}H NMR spectra. The chemical shift (δ=4.30) of the proton signal of the N(1)H$_2$ group of the coordinated trien of **2** was at a higher field than that (δ=4.40) of **1** as shown in Table 1.

Therefore, the N(1)H$_2$ group of **2** is considered to be at a position *trans*[2] to the phenoxyl oxygen of the salicylaldehydato ligand, which is more electronegative than the aldehyde group oxygen.

In addition, the methylene proton signal of **2** was separated to two group signals at δ 2.3—2.7 and 2.7—3.6, and their intensity ratio was 2:10, *i.e.*, two protons of the NH$_2$-side methylene protons at δ 2.4—

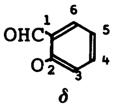


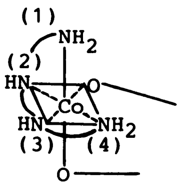
cis-β_1 cis-β_2 cis-α

Fig. 1. The α, β_1, and β_2 configurations of salicylaldehydato(triethylenetetramine)cobalt(III) complex.

TABLE 1. ^{1}H, ^{13}C NMR AND ABSORPTION SPECTRA OF COMPLEXES **1** AND **2**.

^{1}H Complex No.	$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$ δ: NH$_2$-side methylene protons	NH-side methylene protons	$N(1)H_2$	$N(4)H_2$	N(3)H	Salicylaldehydato δ: [N(2)H+ ring protons]	CHO	Absorption bands in methanol λ/nm (ε/cm^{-1} mol^{-1} dm^3)	
1	2.42—3.64(12H)		4.40(2H)	4.98(2H)	6.20(1H)	[6.5—7.6 (5H)]	8.48(1H)$^{a)}$	418(2000)	500(292)
2	2.35—2.75(2H)	2.75—3.57(10H)	4.30(1H)	4.43—4.92(2H) 5.08(1H)	6.15(1H)	[6.5—7.6 (5H)]	8.59(1H)$^{a)}$	418(1830)	500(270)

^{13}C	NH$_2$-side methylene carbons δ		NH-side methylene carbons δ				 δ: c-1	c-2	c-3	c-4	c-5	c-6	CHO
1$^{c)}$	42.7	47.6	48.6	50.2	51.7	52.9	120.2	170.2	118.1	141.6	124.2	137.7	196.7$^{b)}$
2$^{c)}$	42.4	47.6	48.7	50.2	52.2	53.0	120.1	170.0	118.1	141.2	124.4	137.4	196.2$^{b)}$



Solvent and Standard: a) 1.8 mol dm^{-3} D_2SO_4, internal DSS (δ=0), b) D_2O, internal dioxane (δ=67.4).
c) *cf.* Ref. 3, 8 and 9.

2.8 overlap to the NH-side methylene protons at δ 2.8—3.6. While, the methylene proton signal of **1** was not separated to the two group signals. These properties are similar to those of the *cis*-β_2-salicylato(quadridentate amine)cobalt(III) chloride hydrate,[2,3] *cis*-β_2-[Co(sal)L]Cl·nH$_2$O. Thus, the configurations of complexes **2** and **1** have been assigned to *cis*-β_2 and β_1, respectively.

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 270—30 spectrophotometer (Hitachi). The visible absorption spectra were recorded with a Shimadzu UV-210 recording spectrophotometer. The electric conductivities of an aqueous solution were determined by the use of a conductometric meter, CM-30 (Shimadzu), at room temperature.

Preparation of Complexes. Mixture of cis-*β-Salicylaldehydato(triethylenetetramine)cobalt(III) Chloride Dihydrate (1 and 2) and* cis-*β-Salicylato(triethylenetetramine)cobalt(III) Chloride Hydrate (3)*: *cis*-α or β-Dichloro(trien)cobalt(III) chloride (6.0 g, 19.26 mmol) was added to moistend fresh Ag_2O, which was made from silver nitrate (6.54 g, 38.50 mmol) and potassium hydroxide (2.16 g, 38.5 mmol). The mixture was stirred for several minutes at room temperature and then for about 40 min at 60 °C. The precipitated silver chloride was filtered off. The methanol solution (20 cm^3) of salicylaldehyde (2.36 g, 19.32 mmol) was added, drop by drop, to the reddish-violet filtrate. The solution was stirred at room temperature for 50 h and was then concentrated on a rotary evaporator. Then the concentrated solution was injected into a column chromatograph on alumina. On elution of methanol or ethanol, the eluent of the first red band was collected and concentrated. The purification was achieved by a column of ion-exchange resin (SP-Sephadex C-25, Na$^+$ form, 2.5×60 cm). On elution with 0.2 mol dm^{-3} NaCl, the first russet band was assigned to the *cis*-β-salicylato(trien)cobalt(III) chloride hydrate (**3**), and the second orange band (of complexes **1** and **2**) was collected and concentrated on a rotary evaporator. The precipitated NaCl was removed by filtration. Yields: Orange complexes **1** and **2**: 3.2 g (38.4%); russet complex **3**: 1.4 g (18.4%).

Separation of cis-*β_1-Salicylaldehydato(triethylenetetramine)cobalt(III) Chloride Dihydrate (1) and* cis-*β_2-Salicylaldehydato(triethylenetetramine)cobalt(III) Chloride Dihydrate (2)*: The separation of complexes **1** and **2** from the orange complex of 0.5 g was achieved by a column of ion-exchange resin (SP-Sephadex C-25, Na$^+$ form, 2.5×100 cm). On elution with 0.1 mol dm^{-3} NaCl, the effluent of the first orange band (complex **2**) and the second orange band (complex **1**) was collected and concentrated on a rotary evaporator, and the precipitated NaCl was removed by filtration. Yields: 0.13 g for **1**, 0.14 g for **2**. Found **1**: C, 35.90; H, 5.95; N, 12.68; Cl, 15.91%. **2**: C, 36.26; H, 6.52; N, 12.85; Cl, 16.01%. Calcd for $CoC_{13}H_{27}N_4O_4Cl_2$ (MW 433.22) C, 36.04; H, 6.28; N, 12.93; Cl, 16.37%. Dp: 187—189 °C for **1**; 184—185 °C for **2**. Λ=222 for **1**, 213 S cm^2 equiv^{-1} for **2** in water. IR spectra **1**: 1002, 1032, 1059, and 1083 cm^{-1}; 3058, 3100, 3120, 3180, and 3210 cm^{-1}. **2**: 1002, 1035, 1059, and 1080 cm^{-1}; 3082, 3100, 3120, 3190, and 3200 cm^{-1}. Complexes **1** and **2** are very soluble in alcohols, dimethyl sulfoxide, and water, but insoluble in acetone and ether. Both complexes are highly hygroscopic.

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