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Cobalt(III) Complexes with Quadridentate Ligands. XIII.[1] The Preparation and Properties of *cis*-α, *cis*-β_1, and *cis*-β_2-Isomers of the (2-Oxidephenylacetato)(triethylenetetramine)cobalt(III) Complex

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Synopsis. The *cis*-α, *cis*-β_1, and *cis*-β_2-isomers of (2-oxidephenylacetato)(triethylenetetramine)cobalt(III) chloride hydrate, [Co(opa)(trien)]Cl·nH$_2$O (opa=2-oxidephenylacetato, trien=triethylenetetramine), have been prepared and characterized by means of analytical and spectroscopic methods. The *cis*-α and *cis*-β_1-isomers of this complex were more stable than those of the salicylato- or thiosalicylato(triethylenetetramine)cobalt(III) complexes in basic aqueous solution.

In previous papers, we have been concerned with the preparation and properties of isomers of salicylato-,[1—3] thiosalicylato-,[4] salicylaldehydato-,[5] and 8-quinolinolato(triethylenetetramine)cobalt(III) complexes.[6] The cobalt atom of these complexes is wrapped by the five-membered rings of the triethylenetetramine ligand, and by a six-membered ring of a bidentate ligand such as salicylic acid.

Gould[7] reported on the preparation and electron transfer properties of the pentaamminecobalt(III) complex with 2-hydroxyphenylacetic acid as a unidentate ligand, but the mixed-ligand cobalt(III) complex with 2-hydroxyphenylacetic acid as a bidentate ligand (containing a seven-membered ring with a cobalt(III) atom) has not been reported. This paper deals with the preparation and properties of *cis*-α (**1**), *cis*-β_1 (**2**), and *cis*-β_2-(2-oxidephenylacetato)(triethylenetetramine)cobalt(III) complexes (**3**), which contain a seven-membered ring between the cobalt atom and the bidentate 2-oxidephenylacetato ligand. Comparison of the stabilities of these complexes with those of the salicylato- and thiosalicylato(triethylenetetramine)cobalt(III) complexes is also discussed.

Experimental

Measurements. The melting points were measured on a Yanagimoto micro melting point apparatus. The electric conductivities in aqueous solutions were determined by the use of a conductmetric meter CM-40S (Toa) at room temperature. The NMR spectra were recorded with EX-400 and FX-90Q spectrometers (JEOL). The UV spectra in aqueous solutions were recorded with a UV-210 recording spectrophotometer (Shimadzu). The IR spectra were recorded in potassium bromide disks with a 270-30 spectrophotometer (Hitachi).

***cis*-α (1), *cis*-β_1 (2), and *cis*-β_2-(2-Oxidephenylacetato)(triethylenetetramine)cobalt(III) Chloride Hydrate (3).** These complexes were prepared according to the following two methods.

Method 1: To a methanol solution (30 cm^3) of trien (7.3 g, 50 mmol) were added an aqueous solution (2 cm^3) of NaOH (2.0 g, 50 mmol) and then an aqueous solution (10 cm^3) of CoCl$_2$·6H$_2$O (11.9 g, 50 mmol).

After 2-hydroxyphenylacetic acid (7.6 g, 50 mmol) was added to the reaction mixture, air was vigorously introduced into the reaction mixture for 5 h at pH 8.5. The resulting russet solution was warmed to 50 °C for 5 h and then concentrated on a rotary evaporator. The residue was dissolved in methanol, and the solution was passed through a column chromatograph on alumina, then Sephadex LH-20, in order to remove impurities and NaCl. The methanol eluate was concentrated to dryness on a rotary evaporator. A russet solid (10.3 g) was obtained and this residue was dissolved in 10 cm^3 of water. This solution was separated into ten portions and each solution was injected onto a column chromatograph on ion-exchange resin (Dowex 50W-X2, ϕ2.5×60 cm). On elution with 0.3 mol dm^{-3} NaCl, the eluate of the first russet band of complex **3**, that of the second russet band of complex **1**, and that of the third russet band of complex **2** were collected and concentrated on a rotary evaporator. The separated NaCl was removed.

1: Yield 0.8 g (3.6%) as a dark brown powder (from EtOH–Et$_2$O). Mp 194—197 °C. Found: C, 37.29; H, 6.32; N, 13.07; Cl, 8.13%. Calcd for CoC$_{14}$H$_{30}$N$_4$O$_6$Cl (MW 444.81): C, 37.81; H, 6.79; N, 12.59; Cl, 7.98%.

2: Yield 2.3 g (10.8%) as a brown powder (from EtOH–Et$_2$O). Mp 202—204 °C. Found: C, 39.81; H, 6.41; N, 13.77; Cl, 8.98%. Calcd for CoC$_{14}$H$_{28}$N$_4$O$_5$Cl (MW 426.79): C, 39.39; H, 6.61; N, 13.13; Cl, 8.30%.

3: Yield 1.5 g (6.8%) as a reddish-brown powder (from EtOH–Et$_2$O). Mp 213—215 °C. Found: C, 38.30; H, 6.65; N, 12.91; Cl, 8.45%. Calcd for CoC$_{14}$H$_{29}$N$_4$O$_{5.5}$Cl (MW 435.79): C, 38.58; H, 6.70; N, 12.86; Cl, 8.15%.

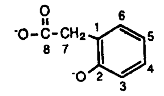
Method 2: The *cis* complexes were prepared from *cis*-α-dichloro(triethylenetetramine)cobalt(III) chloride[8] (6.2 g, 20 mmol) and 2-hydroxyphenylacetic acid (3.04 g, 20 mmol) at pH 10 by Ag$_2$O using previous method,[2] and each isomer was separated according to the same method described above to yield 0.4 g (4.5%) of **1**, 2.9 g (34.0%) of **2**, and 0.9 g (10.3%) of **3**.

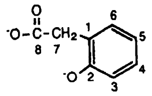
Results and Discussion

(2-Oxidephenylacetato)(triethylenetetramine)cobalt(III) complexes, [Co(opa)(trien)]$^+$, exist in three isomeric forms of *cis*-α, *cis*-β_1, and *cis*-β_2, as shown in Fig. 1. A mixture of *cis*-α (**1**), *cis*-β_1 (**2**), and *cis*-β_2-(2-oxidephenylacetato)(triethylenetetramine)cobalt(III) chloride hydrate (**3**) has been obtained by two methods, and separation of **1**, **2**, and **3** was attempted using an ion-exchange resin.

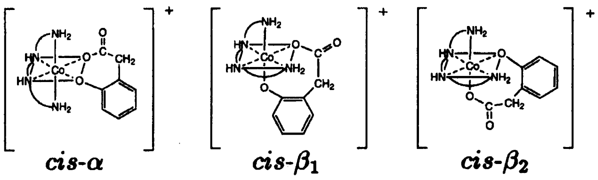
The electric conductivities of **1**, **2**, and **3** in aqueous

Table 1. IR, Absorption, ^{1}H, and ^{13}C NMR Spectra of Complexes **1**—**3**

Complex No.	IR[a)]	Absorption[b)]	^{1}H NMR[c)]							
			CH$_2$	NH$_2$	NH	H-3	H-4	H-5	H-6	H$_2$-7
	cm^{-1}	nm (ε)	δ	δ	δ			δ		
1	1059	350(4820)	2.40—2.85(3H)	5.74(2H)	6.29(1H)	6.94	7.26	6.96	7.22	3.74
	1026	513(402)	2.85—3.00(2H)	5.92(2H)	6.34(1H)					
			3.00—3.54(7H)							
2	1078	353(2730)	2.18—2.35(2H)	4.21(1H)	6.55(1H)	6.94	7.27	6.96	7.22	3.73
	1052	515(300)	2.35—3.52(10H)	4.60(1H)	7.53(1H)					
	1036			5.65(1H)						
	996			6.23(1H)						
3	1092	351(5350)	2.18(4H)	4.28(2H)	6.17(1H)	6.94	7.27	6.96	7.22	3.70
	1053	515(417)	2.71(2H)	5.67(2H)	7.68(1H)					
	1035		3.00(2H)							
	1002		3.15(3H)							
			3.47(1H)							

Complex No.	trien						^{13}C NMR[d)]							
							C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
	δ									δ				
1	42.8	43.4	54.2	55.9	56.2	56.8	131.5	163.9	121.0	129.8	125.3	131.5	41.7	179.7
2	42.3	47.4	48.9	50.0	52.7	53.1	133.0	164.3	121.2	130.3	124.9	131.3	41.6	180.4
3	42.3	47.1	47.5	49.0	52.2	53.0	131.0	164.3	120.8	129.6	124.9	130.0	41.8	180.2

Solvent: a) KBr disk; b) H$_2$O; c) 1.8 mol dm^{-3} D$_2$SO$_4$; d) D$_2$O. Standard: c) DSS; d) Internal dioxane (δ=67.4).



***cis*-α** ***cis*-β$_1$** ***cis*-β$_2$**

Fig. 1. The *cis*-α, β$_1$, and β$_2$ configurations of (2-oxidephenylacetato)(triethylenetetramine)cobalt(III) complex.

solutions were 94, 107, and 107 S cm^2 mol^{-1}, respectively. Buckingham et al., who studied the IR spectra of *cis*-α, *cis*-β$_1$, and *cis*-β$_2$-[Co(gly)(trien)]$^{2+}$ [9)] and many other *cis*-α and *cis*-β-[CoX$_2$(trien)]$^+$ (X=Cl, Br, and NO$_2$) complexes,[10)] reported that the IR spectra of (triethylenetetramine)cobalt(III) complexes showed only two strong peaks for the α-complexes and at least four strong peaks for the β-complexes in the 990—1100 cm^{-1} region due to NH$_2$ twisting of triethylenetetramine. The IR spectrum of **1** showed two strong peaks, and those of **2** and **3** showed four strong peaks in the 990—1100 cm^{-1} region, as shown in Table 1, so that complex **1** was assigned the *cis*-α configuration and complexes **2** and **3** were assigned the *cis*-β configuration.

The absorption spectra of **1**, **2**, and **3** were very similar to each other, as shown in Table 1. The absorption spectra of [Co(sal)(trien)]$^+$ showed absorption bands at 330 (ε=2900) and 513 (205) nm for *cis*-α, 331 (2960) and 530 (270) nm for *cis*-β$_1$, and 333 (3050) and 520 (270) nm for *cis*-β$_2$ as reported previously.[2,3)] The absorption bands of [Co(opa)(trien)]$^+$ at 350—353 nm were assigned to the absorption due to the seven-membered ring with a cobalt atom and 2-oxidephenylacetato ligand. These bands are shifted ca. 20 nm to higher wavelengths compared to the isomers of the [Co(sal)(trien)]$^+$ complexes. The absorption bands at 513—515 nm are assigned to the first d–d absorption bands. This absorption band of **1** is the same as that of *cis*-α-[Co(sal)(trien)]$^+$, but the absorption bands of **2** and **3** are shifted 15 and 5 nm, respectively, to shorter wavelengths compared to *cis*-β$_1$ and *cis*-β$_2$-[Co(sal)(trien)]$^+$ indicating a slightly increased ligand field for 2-oxidephenylacetato complexes compared to salicylato complexes, so that the ligand field strengths may be parallel to the stability of the complexes. No distinction can be made between the isomers on this basis.

In the ^{13}C NMR spectra, the lowest seven signals at δ=120—180 were assigned to the aromatic carbons and carbonyl carbon of the 2-oxidephenylacetato ligand, and the signals at δ=40—60 were assigned to the methylene carbons of the triethylenetetramine and 2-oxidephenylacetato ligands. The methylene carbon signals of **2** and **3** are very similar to each other, but those of complex **1** differ remarkably from those of **2** and **3**, due to the symmetric structure of **1**, as shown in Fig. 2. Thus,

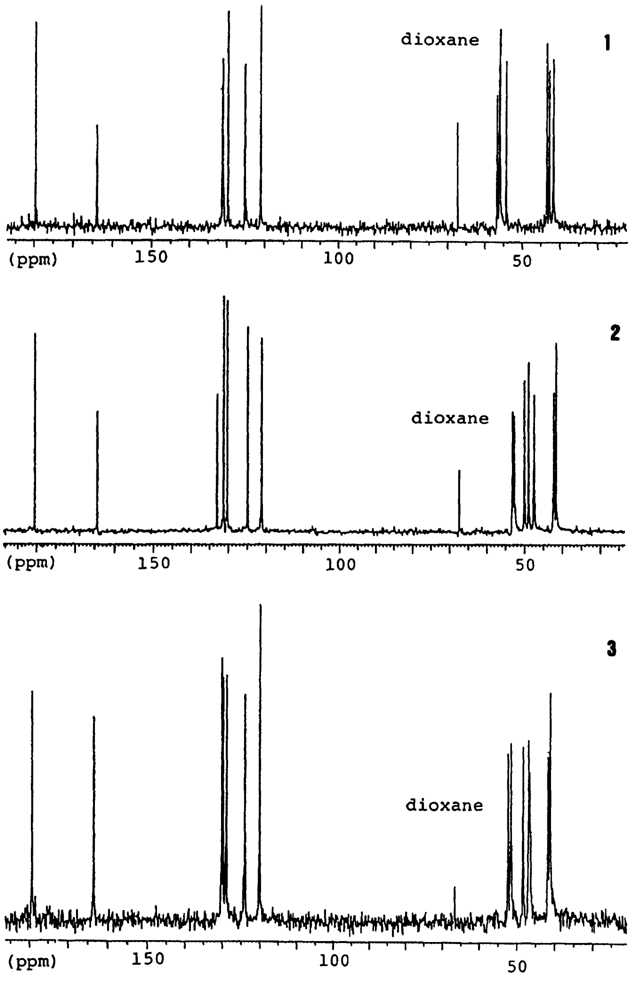


Fig. 2. The ^{13}C NMR spectra of complexes **1**—**3**. **1**: *cis*-α-[Co(opa)trien]Cl·3H_2O, **2**: *cis*-β_1-[Co(opa)-trien]Cl·2H_2O, **3**: *cis*-β_2-[Co(opa)trien]Cl·2.5H_2O. Solvent and standard: D_2O, internal dioxane (δ=67.4).

complex **1** was again distinguished from complexes **2** and **3**, and complex **1** has been assigned to the *cis*-α isomer.

The ^{1}H NMR spectral behaviors of complexes **1**, **2**, and **3** were similar to those of the salicylato- and thiosalicylato(triethylenetetramine)cobalt(III) complexes, which had been reported previously.[1—4] In the ^{1}H NMR spectra of complexes **1**, **2**, and **3** in 1.8 mol dm^{-3} D_2SO_4, as shown in Table 1, the highest field signals at about δ=2.0—3.8 were assigned to the methylene protons, and the signals at δ=6.9—7.3 were assigned to the aromatic protons of the 2-oxidephenylacetato ligand. The signals at δ=5.74(2), 5.92(2), 6.29(1), and 6.34(1) for **1**, at δ=4.21(1), 4.60(1), 5.65(1), 6.23(1), 6.55(1), and 7.53(1) for **2**, and at δ=4.28(2), 5.67(2), 6.17(1), and 7.68(1) for **3** were assigned to the primary and secondary amine protons of the triethylenetetramine ligand. A clear distinction between complexes **2** and **3** was observed in these amine proton signals. The primary amine protons of complex **2** were observed as four separate signals. This observation had been reported in the *cis*-β_1-isomer of the salicylato-[1—3] and thiosalicylato(triethylenetetramine)cobalt(III) complexes.[4] Thus, complex **2** was assigned to the *cis*-β_1-isomer. In addition, the methylene proton signals of **3** were separated to five group signals, whereas the methylene proton signals of **2** were not so separated. These properties are similar to those of the *cis*-β_1 and *cis*-β_2-salicylato-[1—3] and thiosalicylato(triethylenetetramine)cobalt(III) complexes,[4] respectively. Thus, the configurations of complexes **2** and **3** have also been assigned to *cis*-β_1 and *cis*-β_2, respectively.

The property differences between these complexes and the salicylato- and thiosalicylato(triethylenetetramine)cobalt(III) complexes seem to be the different ring size of the coordinated bidentate ligand as follows: i) The *cis*-α-(2-oxidephenylacetato)(triethylenetetramine)cobalt(III) complex (**1**) was obtained from strong basic conditions using Ag_2O (Method 2) and the direct procedure (Method 1), but this isomer (**1**) was unstable in neutral or acidic aqueous solution, and isomerized to the *cis*-β_2-isomer (**3**). This isomerization property was not observed in the *cis*-α-salicylato(triethylenetetramine)cobalt(III) complex. ii) The *cis*-β_1-isomer of the (2-oxidephenylacetato)(triethylenetetramine)cobalt(III) complex (**2**) was obtained in the largest amounts of the three possible isomers, and slowly isomerized to the *cis*-β_2-isomer (**3**) in acidic aqueous solution. But *cis*-β_1-salicylato(triethylenetetramine)cobalt(III) complex was the most unstable isomer of the three possible isomers and only a vely small amount was obtained.[2] This isomer was easily isomerized to the *cis*-β_2-isomer, while the *cis*-β_1 and *cis*-β_2-isomers of the thiosalicylato(triethylenetetramine)-cobalt(III) complex were observed as reversible isomeric tautomers.[4] iii) The *cis*-β_2-isomer (**3**) was the most stable isomer of the three possible isomers, but this isomer (**3**) was obtained in a smaller amount than the *cis*-β_1-isomer (**2**) in basic reaction media. iv) The absorption bands near 350 nm in the absorption spectra of **2** and **3** differ remarkably from the corresponding salicylato complexes.

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