Preparation and Properties of "β_1 and β_2"-Isomers of the Salicylato(triethylenetetramine)cobalt(III) Complex

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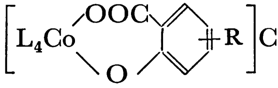
β-Salicylato(triethylenetetramine)cobalt(III) chloride monohydrate has been obtained from salicylic acid and β-dichloro(triethylenetetramine)cobalt(III) chloride at pH 10—11. The separation of "β_1 and β_2" isomers was attempted by using ion exchange. The IR spectra of the "β_1 and β_2" complexes showed four strong absorption peaks in the 990—1100 cm^{-1} region. This indicates that the complexes assume the β-form. The ^{1}H-NMR spectrum of ammine protons of coordinated triethylenetetramine of the β_1 complex showed six signals with an intensity ratio of 1:1:1:1:1:1, while that of the β_2 complex showed five signals with an intensity ratio of 1:1:1:1:2, in 1.8 mol dm^{-3} D_2SO_4. The order of the chemical shifts in ppm is $N(2)H<N(3)H<N(4)H_2<N(1)H_2$. Thus, the protons of the secondary N(3)H of coordinated triethylenetetramine absorb at lower fields than the terminal $N(1)H_2$ protons. The ^{13}C-NMR spectra of the "β_1 and β_2" complexes in heavy water showed six signals for trien-ligand carbons and seven signals for salicylato-ligand carbons. The spectra of these complexes have shown two different configurations of the "β_1 and β_2" complexes.

The preparation[1-3] and some properties[3-6] of salicylato- or cresotinato(tetraammine)cobalt(III) chloride monohydrate and aslicylato- or cresotinatobis(ethylenediamine)cobalt(III) chloride dihydrate with the formula of  (L: NH_3, L_2: en, R: H, CH_3) have already been reported. The present paper deals with the isolation of β_1 and β_2 isomers of salicylato(triethylenetetramine)cobalt(III) chloride monohydrate[7] and their properties.

As far as the present authors know, no report has appeared on the configuration of a cobalt(trien) complex which is chelated by two oxygen atoms as in the present example, although studies of the stereochemistry of the $[Co(trien)(amino\text{-}acidato)]^{2+}$ complex (trien=triethylenetetramine, amino-acidato=glycinato, sarcosinato···) have been reported by some authors.[8,9]

Results and Discussion

Complexes. Three isomeric forms are possible for the salicylato(triethylenetetramine)cobalt(III) complex, as is shown in Fig. 1. A mixture of β_1 and β_2-salicylato(triethylenetetramine)cobalt(III) chloride monohydrate was obtained from salicylic acid and β-dichloro(triethylenetetramine)cobalt(III) chloride at pH 10—11. The separation of the isomers was achieved by the use of ion-exchange resin. Attempts to obtain the α-form using α-dichloro(triethylenetetramine)cobalt(III) chloride invariably resulted in the isolation of a mixture of the β_1 and β_2-forms at pH 2—8. The α-form may, then, be thermodynamically unstable.[10] The α-glycinato(triethylenetetramine)cobalt(III) chloride can not be prepared at pH 7—8,[10,11] but it can be prepared at pH 3[11] from glycine and α-dichloro(triethylenetetramine)cobalt(III) chloride.

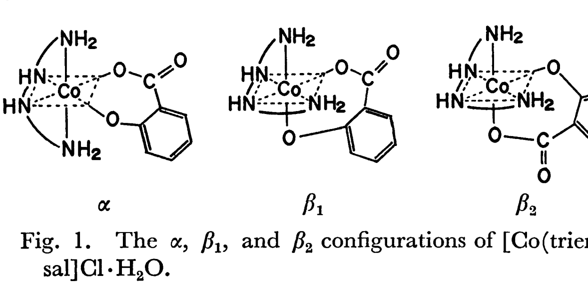
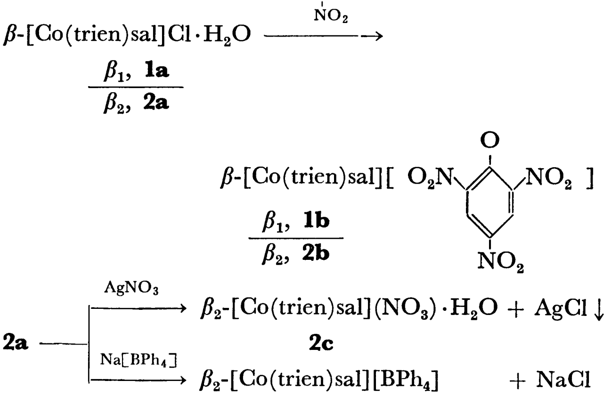


Fig. 1. The α, β_1, and β_2 configurations of [Co(trien)sal]Cl·H_2O.

The β_1 and β_2-salicylato(triethylenetetramine)cobalt(III) picrate complexes have been prepared



from picric acid and the corresponding chloride monohydrate. The β_1 and β_2 chloride monohydrate complexes (hereafter denoted as **1a** and **2a** respectively) are russet, while the corresponding picrates (denoted by **1b** and **2b** respectively) are orange. They are insoluble in most organic solvents, but the **1a** and **2a** complexes are soluble in water, methyl alcohol, and dimethyl sulfoxide. Salicylato(triethylenetetramine)cobalt(III) nitrate monohydrate (**2c**) has been prepared from silver nitrate and the corresponding chloride monohydrate (**2a**). It is russet and soluble in water. The corresponding tetraphenyl borate (**2d**) has been prepared from sodium tetraphenyl borate and the **2a** complex. It is pink and soluble in acetone and dimethyl sulfoxide. When the **1a** and **2a** complexes are treated with 60% nitric acid, very deep green solutions are formed. They should contain complexes[3-6] similar to $[CoL_4 5\text{-}NO_2sal]^{2+}$ (L: NH_3, L_2:

en). The **1a** and **2a** complexes are diamagnetic and should be a cobalt(III) complex of the low-spin type. The absorption spectra of the **1a**, **1b**, **2a**, **2b**, **2c**, and **2d** complexes are collected in Table 1.

IR Spectra. Buckingham *et al.*, who studied the IR spectra of α, β_1, and β_2-[Co(trien)gly]$^{2+}$,[9,10] reported that the IR spectra of (trien)cobalt(III) complexes showed at least two strong absorption bands for α-complexes and at least four strong absorption bands for β-complexes in the 990—1100 cm^{-1} region. They also reported that the IR spectra of α-complexes showed three absorption bands, while those of β-complexes showed more complicated and usually four strong (and, in some cases, five) absorption bands, in the 3000—3300 cm^{-1} region.[12] The IR spectra of the **1a** and **2a** complexes have four strong peaks in the 990—1100 cm^{-1} region (Table 1) and four peaks in the 3000—3300 cm^{-1} region; *i.e.*, the IR spectrum of the **1a** complex has peaks at 2950, 3075, 3150, 3220, and 3275(sh), and that of the **2a** complex has peaks at 2875, 2950, 3050, 3150(sh), 3200, and 3275(sh), which is the shift on deuteration[12] to 2250—2450 cm^{-1}. This indicates that the complexes assume the β-form. The IR spectral data of the **1a**, **1b**, **2a**, **2b**, **2c**, and **2d** complexes are collected in Table 1.

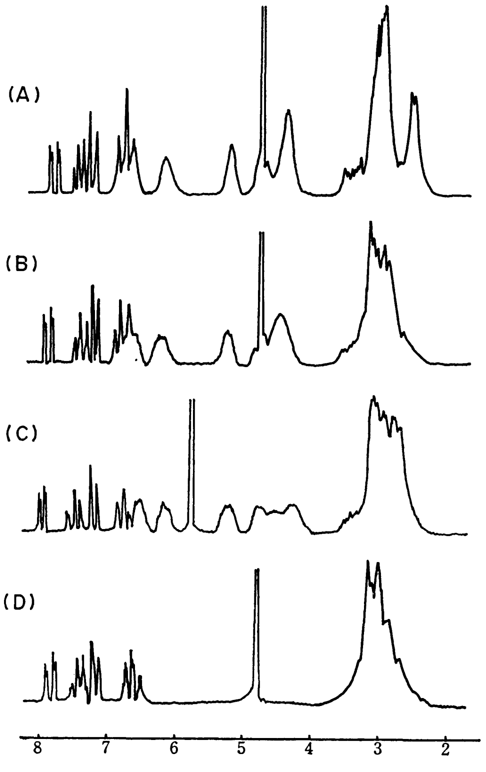
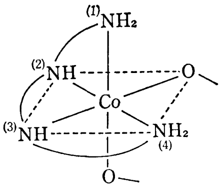


Fig. 2. The ^{1}H-NMR spectra of **1a** and **2a** complexes. (A): β_2-[Co(trien)sal]Cl·H_2O in 0.1mol dm^{-3} D_2SO_4. (B): β_1-[Co(trien)sal]Cl·H_2O in 0.1mol dm^{-3} D_2SO_4. (C): β_1-[Co(trien)sal]Cl·H_2O in 1.8 mol dm^{-3} D_2SO_4. (D): β_1-[Co(trien)sal]Cl·H_2O in heavy water containing NaOH. Standard: internal DSS.



N(1), N(2), N(3), and N(4) of coordinated trien ligand.

NMR Spectra. The ^{1}H-NMR spectra of the **1a** and **2a** complexes were measured in 0.1 mol dm^{-3} DCl, 0.1 mol dm^{-3} D_2SO_4, and 1.8 mol dm^{-3} D_2SO_4. In Fig. 2, the signals (2.3—3.8 ppm, 12H) at the highest field are assigned to the methylene protons of the coordinated trien. The signals of 4.0—6.7 ppm are assigned to the protons of the NH and NH_2 group. The multiplet (6.5—8.2 ppm) at the lowest field is assigned to the protons of the salicylato ligand. The signal of the methylene protons of the coordinated trien of the **1a** complex showed one peak, and that of **2a** showed two peaks in the 2.3—3.8 ppm region, as is shown in Fig. 2 and Table 1. The protons of both the NH and NH_2 groups of the coordinated trien of the **1a** and **2a** complexes showed five signals in the intensity ratio of 1 : 1 : 1 : 1 : 2 in 0.1 mol dm^{-3} D_2SO_4 or in 0.1 mol dm^{-3} DCl. They disappeared in heavy water containing NaOH. Buckingham *et al.* reported that the order of chemical shifts in ppm is $NHR_1R_2 < NH_2R < NH_3$.[11,13] Thus, in β_1 and β_2 also, the proton of the secondary NH of coordinated trien is considered to absorb at lower fields than the terminal NH_2 protons. Marzilli and Buckingham[10] also found that, in the spectra of the β_2-[Co(trien)sar]$^{2+}$ ion, the NH_2 protons in a position *trans* to the coordinated carboxyl oxygen of the sarcosinato ligand absorb at a higher field than those in a position *cis* to the coordinated carboxyl oxygen. If the same relation holds in our β_1 and β_2 complexes, the N(1)H_2 protons of coordinated trien is thought to absorb at a higher field than the N(4)H_2 protons, while the N(3)H proton probably absorbs at a higher field than the N(2)H proton, because N(1) and N(3) are at positions *trans* to the coordinated carboxyl oxygen or phenoxy oxygen.[6] Thus, the order of the ^{1}H chemical shifts in ppm should be: $N(2)H < N(3)H < N(4)H_2 < N(1)H_2$. Now, in the [Co-$(NH_3)_4$sal]$^+$ ion[6] it has been found that the NH_3 protons in a position *trans* to the coordinated carboxyl

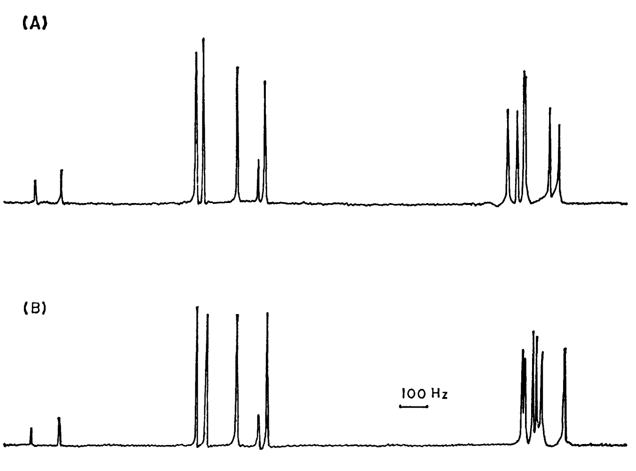
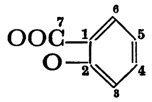


Fig. 3. The ^{13}C-NMR spectra of **1a** and **2a** complexes in D_2O. (A): β_1-[Co(trien)sal]Cl·H_2O. (B): β_2-[Co(trien)sal]Cl·H_2O.

TABLE 1. ^{1}H-, ^{13}C-NMR SPECTRA AND SOME PROPERTIES

Complex	^{1}H-NMR spectra					
	$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$					
	CH_2 δ/ppm		$N(1)H_2$ δ/ppm	$N(4)H_2$ δ/ppm		$N(3)H$ δ/ppm
1a	2.35—3.72(12H)		4.43(2H)	a)	5.24(1H)	6.25(1H)
	2.39—3.89(12H)		4.50(2H)	a)	5.29(1H)	6.29(1H)
	2.39—3.76(12H)		4.34(1H) 4.57(1H)	4.81(1H)	5.23(1H)	6.20(1H)
	2.30—3.83(12H)					
1b	2.31—3.85(12H)		4.40(2H)	4.80(1H)	a)	6.15(1H)
2a	2.31—2.78(3H)	2.78—3.68(9H)	4.31(2H)	a)	5.23(1H)	6.18(1H)
	2.30—2.76(3H)	2.76—3.80(9H)	4.40(2H)	a)	5.25(1H)	6.19(1H)
	2.38—2.80(3H)	2.80—3.80(9H)	4.34(2H)	4.76(1H)	5.21(1H)	6.07(1H)
	2.35—2.79(3H)	2.79—3.73(9H)				
2b	2.33—2.74(3H)	2.74—3.81(9H)	4.32(2H)	4.77(1H)	a)	6.08(1H)
2c	2.28—2.85(3H)	2.85—3.76(9H)	4.36(2H)	4.71(1H)	5.18(1H)	6.03(1H)
2d						
3						

	^{13}C-NMR spectra												
	$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$												
							C-1	C-2	C-3	C-4	C-5	C-6	C-7
1a	46.6	45.8	51.9	52.1	53.9	56.9	118.6	167.8	117.4	134.3	124.2	132.4	174.6[8]
2a	42.0	47.5	48.3	49.7	52.1	52.7	118.1	168.2	117.1	134.5	124.3	132.3	174.1[8]
2c	42.0	47.4	48.3	49.8	52.1	52.6	117.0	168.3	118.4	134.5	124.3	132.3	174.1[8]
3							117.5	167.5	117.5	134.6	124.1	132.7	174.1[9]

oxygen of the salicylato ligand absorb at the highest field. As for the **1a** and **2a** complexes in a 0.1 mol dm^{-3} D_2SO_4 solution, the chemical shift (4.40 ppm) of the proton signal of the $N(1)H_2$ group of the **2a** complex is at a higher field than that (4.50 ppm) of the **1a** complex, as is shown in Fig. 2 and Table 1. Therefore, the $N(1)H_2$ group of the **2a** complex is considered to be at a position *trans* to the carboxyl oxygen of the salicylato ligand, which is more electronegative than the phenoxy oxygen.[6] Thus, the **2a** and **1a** complexes can be assigned to β_2 and β_1 respectively.

In the 1.8 mol dm^{-3} D_2SO_4 solution, the spectrum of the **1a** complex showed six peaks with an intensity ratio of 1 : 1 : 1 : 1 : 1 : 1, while that of the **2a** complex showed five peaks with an intensity ratio of 1 : 1 : 1 : 1 : 2. The signal at 4.50 ppm of the highest field, based on the $N(1)H_2$-group protons of the coordinated trien of the **1a** complex, split into two signals at 4.34 and 4.57 ppm. This seems to be a result of the formation of hydrogen bonding[14] between the carbonyl oxygen of the salicylato ligand and protons of sulfuric acid. The carbonyl oxygen of the coordinated salicylato of the **1a** complex is near to the $N(1)H_2$ protons in a position *trans* to the coordinated phenoxy oxygen of that complex. This is also in harmony with the assignment of the **1a** complex assuming it to have the β_1 form.

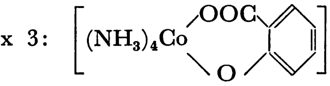
In the ^{13}C-NMR spectra of the **1a** and **2a** complexes in heavy water, there have been observed six signals for the trien ligand and seven signals for the salicylato ligand. The chemical shifts of the salicylato ligands of the **1a** and **2a** complexes agreed with each other, but those of the trien ligand were different, as is shown in Fig. 3 and Table 1. The chemical shifts of the salicylato ligand are assigned on the basis of the chemical shift of the salicylato(tetraammine)cobalt(III) chloride monohydrate.[6] Those of the trien ligand are difficult to assign to the individual carbon atom. They have shown the two different configurations of the β_1 and β_2 complexes. The NMR spectral data of the **1a**—**1b** and **2a**—**2c** complexes are collected in Table 1.

OF **1a**, **1b**, **2a**, **2b**, **2c**, AND **2d** COMPLEXES

[N(2)H+salicylato] δ/ppm		(picrate) δ/ppm	IR spectra		Absorption bands		Electric conductivity of aqueous solution
N(2)H δ/ppm	(salicylato) δ/ppm		990—1100 cm^{-1}	$\rho_r(NH_{(2)})_r$ cm^{-1}	nm	ε	S cm^2 eq^{-1}
[6.49—7.95(5H)]$^{1)}$			999, 1030	835	331	2960$^{6)}$	93
[6.56—7.99(5H)]$^{2)}$			1060(vs), 1080(s)		530	270	
6.51(1H)	6.66—8.00(4H)$^{3)}$						
	6.75—7.90(4H)$^{4)}$						
[6.48—7.99(5H)]$^{5)}$		9.20(2H)	1000, 1028	838	520	275$^{6)}$	
			1060(vs), 1075(vs)$^{b)}$				
[6.51—7.94(5H)]$^{1)}$			990, 1030	835	333	3050$^{6)}$	124
[6.50—7.94(5H)]$^{2)}$			1060(s), 1075(vs)		520	270	
[6.49—7.97(5H)]$^{3)}$							
	6.62—7.93(4H)$^{4)}$						
[6.50—7.92(5H)]$^{5)}$		9.22(2H)	1005, 1030	838	510	290$^{6)}$	
			1060(s), 1075(vs)				
[6.48—7.99(5H)]$^{3)}$			990, 1030	835	333	2970$^{6)}$	
			1050(s), 1075(vs)		511	273	
			990, 1030	845	333	2600$^{7)}$	
			1048(s), 1068(vs)		522	274	
				840	330	2900$^{6)}$	
					533	160	

Solvent: 1) 0.1 mol dm^{-3} DCl, 2) 0.1 mol dm^{-3} D_2SO_4, 3) 1.8 mol dm^{-3} D_2SO_4, 4) 0.1 mol dm^{-3} NaOH and D_2O, 5) 0.9 mol dm^{-3} D_2SO_4, 6) H_2O, 7) Acetone, 8, 9) D_2O.

Standard: 1)—5) internal DSS, 8) internal dioxane ($\delta=67.4$), 9) intermal MeOH ($\delta=49.8$ ppm).

Complex 3:  Cl·H_2O, Ref. 6.

a) This signal overlapped with each solvent. b) This signal overlapped with picric acid.

Experimental

Measurements. The NMR spectra were recorded with a FX-60 apparatus (JEOL) for ^{13}C-NMR and an R-40 apparatus (Hitachi) for ^{1}H-NMR. The IR spectra were recorded in potassium bromide disks with a IR-27G apparatus (Shimadzu). The visible absorption spectra were recorded with a Shimadzu MPS-5000 recording spectrophotometer. The magnetic susceptibilities were measured by the Gouy method using a magnetic balance (Shimadzu) at room temperature. The pH was measured with a Toa Electronics pH-meter HM-5B. The electric conductivity of an aqueous solution were determined by the use of a conductometer, CM-30 (Shimadzu), at room temperature.

Preparation of Complexes. *β-Salicylato(trien)cobalt(III) Chloride Monohydrate*: This complex was prepared from β-dichloro(trien)cobalt(III) chloride[15] (46 g, 148 mmol dm^{-3}) and salicylic acid (20.5 g, 148 mmol dm^{-3}) at pH 10—11 by Morgan's method[2] and was then recrystallized from water. Yield: 40.46 g (69.3%).

Separation of β_1-Salicylato(trien)cobalt(III) Chloride Monohydrate (1a) and β_2-Salicylato(trien)cobalt(III) Chloride Monohydrate (2a): Five-tenths of a gram of β-[Co(trien)sal]Cl·H_2O was dissolved in 1.5 ml of water, and the solution was passed through a large column of cation-exchange resin (2.5×50 cm, Dowex 50W-X2). Two red bands separated on elution with a 0.3 mol dm^{-3} NaCl solution. The solution of the first band (**1a**) and that of the second band (**2a**) were concentrated in a rotary evaporator, and the NaCl was removed by filtration. The **1a** and **2a** complexes were both recrystallized from water. Yields: 0.022 g (4.4%) for **1a**; 0.42 g (84%) for **2a**; Found **1a**: C, 39.47; H, 6.07; N, 14.45; Cl, 8.76%. **1b**: C, 39.68; H, 6.14; N, 14.39; Cl, 9.00%. Calcd for $CoC_{13}H_{24}N_4O_4Cl$: (*MW* 394.75) C, 39.56; H, 6.13; N, 14.19; Cl, 8.98%.

β_1-Salicylato(trien)cobalt(III) Picrate (1b) and β_2-Salicylato(trien)cobalt(III) Picrate (2b): An aqueous solution of the **1a** or **2a** complex (0.5 g, 1.27 mmol dm^{-3}) was added to a solution of picric acid (0.29 g, 1.27 mmol dm^{-3}), the mixture was stirred, and the separated orange complex was filtered and recrystallized from water. Yields: 0.36 g (50%) for **1b**; 0.42 g (58.2%) for **2b**; Found **1b**: C, 39.99; H, 4.63; N, 16.96%. **2b**: C, 40.24; H, 4.46; N, 17.06%. Calcd for $CoC_{19}H_{24}N_7O_{10}$: (*MW* 569.37) C, 40.08; H, 4.25; N, 17.22%.

β_2-Salicylato(trien)cobalt(III) Nitrate Monohydrate (2c): An aqueous solution of silver nitrate (0.45 g, 2.65 mmol dm^{-3}) was added to an aqueous solution of **2a** (1.0 g, 2.53 mmol dm^{-3}), the mixture was stirred, and the precipitated silver chloride was filtered. The filtrate was concentrated and recrystallized from water as russet crystals. Yield: 0.65 g (60.9%); Found: C, 37.29; N, 5.67; N, 16.56%. Calcd for $CoC_{13}H_{23}N_5O_7$: (*MW* 421.30) C, 37.06; H, 5.74; N, 16.62%.

β_2-Salicylato(trien)cobalt(III) Tetraphenylborate (**2d**): An aqueous solution of the **2a** complex (1.0 g, 2.53 mmol dm^{-3}) was added to a solution (0.95 g, 2.78 mmol dm^{-3}) of sodium tetraphenylborate, the mixture was stirred, and the precipitated pink complex was filtered off and washed with water, and ethanol and dried *in vacuo*. Yield: 1.45 g (86.7%); dec 216 °C, Found: C, 67.12; H, 6.60; N, 8.58%. Calcd for $CoC_{37}H_{42}N_4O_3B$: (*MW* 660.51) C, 67.28; H, 6.41; N, 8.48%.

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