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Mixed-ligand Schiff Base Cobalt(III) Complexes with Phenolaldehydes or Phenolketones as Ligands

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Abstract

Mixed-ligand cobalt(III) complexes of the type [Co(L)(SB)] were prepared and characterized, where L is an aldehyde- or ketone-phenolate anion such as salicylaldehydate (sal), 5-chlorosalicylaldehydate (5-Cl-sal), 3,5-dichlorosalicylaldehydate (3,5-Cl-sal), or *o*-hydroxyacetophenonate (oap), whereas SB is a deprotonated Schiff base anion such as *N,N'*-disalicylideneethylenediaminate (sal$_2$en), *N,N'*-disalicylidene-1,3-propanediaminate (sal$_2$tn), *N,N'*-bis(7-methylsalicylidene)ethylenediaminate (7,7'-Me-sal$_2$en), or *N,N'*-bis(7-ethylsalicylidene)-1,3-propanediaminate (7,7'-Me-sal$_2$tn). For SB = sal$_2$en and sal$_2$tn, two isomers each were obtained as green and brown crystals; both exhibited, however, the same ^{1}H NMR and absorption spectra in methanol, chloroform or dichloromethane. On the other hand, only the green form has thus far been obtained for SB = 7,7'-Me-sal$_2$en and 7,7'-Me-sal$_2$tn. X-ray analysis of a single crystal of [Co(sal)(7,7'-Me-sal$_2$tn)] has shown that two phenolato-oxygens of the Schiff base in the complex are in the *cis* position, and the three phenolate-oxygen atoms including that of the salicylaldehydato are situated in meridional position. The Co–O (aldehyde) distance was found to be longer than the Co–O (phenolato) distance in the above complex and also the Co–O distances in amino acid complexes. The stability of the possible geometric structures of the complexes has been examined on the basis of conformational analysis.

Introduction

Schiff bases are in general very able coordinating ligands and at the same time have certain peculiarities. Thus they form very stable cobalt(II) complexes which are often quite resistant to oxidation, and the information on the cobalt(III) Schiff base complexes which are mostly mixed-ligand complexes, is still quite limited [1–4]. Such cobalt(III) complexes are in general obtained by the air-oxidation of cobalt(II) Schiff base complexes in the presence of additional ligands such as acetylacetone or amino acids [5]. The present authors were first interested in the phenomenon that Schiff base cobalt(II) complexes are dissolved in chloroform or dichloromethane in contact with air even without the additional ligands, and by chromatography of such solutions they could isolate mixed-ligand complexes containing salicylaldehyde together with small quantities of binuclear Schiff base cobalt(III) complexes. The salicyladehyde was probably produced by the decomposition of the Schiff base ligand. Since complexes having aldehyde as ligands were novel ones at that time, the authors promoted the research of such mixed-ligand complexes of various aldehydes or ketones and Schiff bases by establishing their direct synthetic route, and inquired into their fundamental characteristics. The present paper deals mainly with the syntheses, X-ray crystal analysis, ^{1}H NMR and absorption spectra, TG–DTA data and conformational analysis of the possible isomers of such mixed-ligand complexes.

Experimental

Preparation of Ligands

The Schiff base ligands were prepared according to the manner reported by Hariharan and Urbach [6], *i.e.* by refluxing aldehyde or ketone and the diamine in 2:1 molar ratio in methanol, and recrystallizing the yellow products in methanol. In the case of *N,N'*-bis(7-methylsalicylidene)-1,3-propanediamine, preparation was conducted at room temperature.

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Preparation of Cobalt(II) Schiff Base Complexes

These were also prepared according to the procedure described by Hariharan and Urbach [6]. *N,N'*-bis(7-methylsalicylidene)-1,3-propanediaminatocobalt(II)hydrate, [Co(7,7'-Me-sal$_2$tn9]·1.5H_2O was likewise obtained with a yield of about 7.4 g in 0.02 molar scale of the preparation. *Anal.* Found: C, 57.49; H, 5.28; N, 7.06. Calc. for [Co(7,7'-Me-sal$_2$tn)]·1.5H_2O: C, 57.86; H, 5.89; N, 7.11%.

Preparation of Co(III)(aldehyde-phenolato) (Schiff Base) and Co(III)(ketone-phenolato) (Schiff Base) Complexes

[Co(sal)(sal$_2$tn)] (brown form, Ia)

To the mixture of the [Co(sal$_2$tn)]·2H_2O (3 g, 0.008 mol) and methanol (120 ml) was added salicylaldehyde (4 g, 0.033 mol) with stirring. The brownish fine precipitates obtained when the mixture was kept at 30 °C on a water bath for 60 min were dried under reduced pressure after washing with diethyl ether. Yield, 3 g. *Anal.* Found: C, 62.20; H, 4.68; N, 6.07. Calc. for [Co(sal)(sal$_2$tn)]: C, 62.47; H, 4.68; N, 6.08%.

[Co(sal)(sal$_2$tn)]·H_2O (green form, Ib)

To the mixture of salicylaldehyde (1.0 g, 0.0082 mol) and methanol (40 ml) was added [Co(sal$_2$tn)]·2H_2O (1.0 g, 0.0027 mol) little by little with stirring on a water bath at 55 °C for 30 min. After the reaction mixture was filtered with a glass filter, the filtrate was concentrated to one-fifth of its original volume under reduced pressure at room temperature. A green precipitate was obtained by the addition of petroleum ether and diethyl ether to the concentrated filtrate. It was dried under reduced pressure after washing with diethyl ether. This green complex could also be obtained by the addition of petroleum ether to a chloroform solution of the brown-form complex **Ia** prepared above. *Anal.* Found: C, 60.26; H, 4.56; N, 5.86. Calc. for [Co(sal)(sal$_2$tn)]·H_2O: C, 60.25; H, 4.86; N, 5.86%.

[Co(5-Cl-sal)(sal$_2$tn)]·0.5H_2O (brown form, IIa)

The brownish crystalline powder of the desired complex was prepared by adding 5-chlorosalicylaldehyde (0. 9g, 0.0054 mol) with stirring to a mixture of [Co(sal$_2$tn)]·2H_2O (1.0 g, 0.0027 mol) and methanol (40 ml) at room temperature. The reaction mixture was stirred for 70 min, and then the filtered complex was washed with petroleum ether and diethyl ether, and dried under reduced pressure. Yield, 1.2 g. *Anal.* Found: C, 57.21; H, 4.21; N, 5.56. Calc. for [Co(5-Cl-sal)(sal$_2$tn)]·0.5H_2O: C, 57.18; H, 4.06; N, 5.44%.

[Co(3,5-Cl-sal)(sal$_2$tn)] (brown form, IIIa)

To the mixture of [Co(sal$_2$tn)]·2H_2O (1.0 g, 0.0027 mol) and methanol (40 ml) was added with stirring 3,5-dichlorosalicylaldehyde (1.0 g, 0.0052 mol), and stirring was continued for about 35 min at room temperature. The reaction mixture was filtered with a glass filter and the filtrate was concentrated to half the volume of the original solution under reduced pressure at 30 °C. The brownish powder crystals precipitated were washed with petroleum ether and diethyl ether, and then dried under reduced pressure. Yield, 0.9 g. *Anal.* Found: C, 54.03; H, 3.66; N, 5.21. Calc. for [Co(3,5-Cl-sal)(sal$_2$tn)]: C, 54.46; H, 3.63; N, 5.29%.

[Co(oap)(sal$_2$tn)]·0.25H_2O (brown form, IVa)

To the mixture of *o*-hydroxyacetophenone (1.0 g, 0.0073 mol) and methanol (20 ml) was added [Co(sal$_2$tn)]·2H_2O (1.3 g, 0.0035 mol) little by little with stirring in methanol (40 ml) on a water bath at 55 °C and stirring was continued for about an hour. The reaction mixture was then filtered with a glass filter. Brownish powder precipitate of the desired complex was obtained after the filtrate was concentrated up to about a quarter of the volume under reduced pressure at room temperature. The product was dried under reduced pressure after washing with petroleum ether and diethyl ether. Yield, 1.1 g. *Anal.* Found: C, 62.98; H, 4.96; N, 5.98. Calc. for [Co(oap)(sal$_2$tn)]·0.25H_2O: C, 62.69; H, 4.96; N, 5.85%.

[Co(oap)(sal$_2$tn)]·H_2O (green form, IVb)

The green form complex was obtained by adding diethyl ether and petroleum ether to a chloroform solution of the brown form complex (**IVa**) obtained above. *Anal.* Found: C, 60.97; H, 4.72; N, 5.69. Calc. for [Co(oap)(sal$_2$tn)]·H_2O: C, 60.97; H, 4.85; N, 5.77%.

β_2-[Co(sal)(7,7'-Me-sal$_2$tn)] (dark green form, Vb)

The salicylaldehyde (0.9 g, 0.0074 mol) was added with stirring to [Co-(7,7'-Me-sal$_2$tn)]·1.5H_2O (1.1 g, 0.0028 mol) suspended in about 60 ml of methanol. The mixture was heated at 55 °C, on a water bath with stirring for 30 min. After the reaction mixture was once filtered with a glass filter, the filtrate was concentrated under reduced pressure at 30 °C; the dark green complex was obtained from the concentrated solution and dried under reduced pressure after washing with diethyl ether. Yield, 1.2 g. A needle crystal obtained by recrystallizing the complex in a 2:1 mixture of dichloromethane and acetonitrile was used for X-ray analysis. *Anal.* Found: C, 63.68; H, 5.27; N, 5.91. Calc. for [Co(sal)(7,7'-Me-sal$_2$tn)]: C, 63.93; H, 5.17; N, 5.74%.

[Co(oap)(7,7'-Me-sal$_2$tn)]·0.5H$_2$O (green form, VIb)

To *o*-hydroxyacetophenone (1.1 g, 0.0080 mol) in 30 ml of methanol was added with stirring [Co(7,7'-Me-sal$_2$tn)]·1.5H$_2$O (1.3 g, 0.0033 mol) at room temperature to produce the desired green complex. Further crops of the same green complexes were obtained by adding petroleum ether to the mother liquor after concentration under reduced pressure at 25–30 °C. The complex obtained was dried under reduced pressure after washing with diethyl ether. Total yield, 1.2 g. *Anal.* Found: C, 63.53; H, 5.51; N, 5.57. Calc. for [Co(oap)(7,7'-Me-sal$_2$tn)]·0.5H$_2$O: C, 63.40; H, 5.53; N, 5.48%.

[Co(sal)(sal$_2$en)]·H$_2$O (brown form, VIIa)

Salicylaldehyde (1 g, 0.0082 mol) was added with stirring to [Co(sal$_2$en)] (1 g, 0.0031 mol, dark-violet crystal) suspended in 25 ml of methanol at 55 °C on a water bath. After 30 min, the solution changed to dark brown and the brownish compound was produced. Yield, 1.2 g. *Anal.* Found: C, 59.79; H, 4.80; N, 5.90. Calc. for [Co(sal)(sal$_2$en)]·H$_2$O: C, 59.48; H, 4.57; N, 6.03%.

[Co(sal)(sal$_2$en)]·0.5H$_2$O (green form, VIIb)

This green complex also was obtained by adding petroleum ether to the solution of the brown form complex of [Co(sal)(sal$_2$en)]·H$_2$O (*VIIa*) in chloroform. *Anal.* Found: C, 59.96; H, 4.31; N, 6.63. Calc. for [Co(sal)(sal$_2$en)]·0.5H$_2$O: C, 60.66; H, 4.44; N, 6.15%.

[Co(sal)(7,7'-Me-sal$_2$en)] (green form, VIIIb)

To a suspension of [Co(7,7'-Me-sal$_2$en)]·0.5H$_2$O (3.0 g, 0.0085 mol) in 50 ml of methanol was added salicylaldehyde (3.0 g, 0.025 mol) with stirring at 50 °C on a water bath for *ca.* 80 min. The green complex obtained was dried under reduced pressure at 60 °C after washing with methanol, a 1:1 solution of methanol and diethyl ether, and then with diethyl ether. Yield, 3.5 g. *Anal.* Found: C, 63.01; H, 4.88; N, 6.01. Calc. for [Co(sal)(7,7'-Me-sal$_2$en)]: C, 63.30; H, 4.88; N, 5.90%.

Silica-gel Column Chromatography of the Air-oxidation Mixture of a Schiff Base and Cobalt(II) Chloride

To a mixed solution of *N,N'*-bis(salicylaldehyde)-1,3-propanediamine (5.6 g, 0.02 mol) and triethylamine (4.8 g, 0.0047 mol) in 400 ml of methanol, the solution of cobalt(II) chloride hexahydrates (4.8 g, 0.020 mol) in 200 ml of water was added and oxidized by air-bubbling for 30 min at room temperature. The green product separated on a glass filter was extracted with dichloromethane and a green precipitate was obtained by concentration under reduced pressure. Yield, 4.6 g.

The green product (1.0 g) obtained above dissolved in 30 ml of dichloromethane was chromatographed on silica-gel (Merk, 60F$_{254}$) packed into a column (30 (dia.) × 510 mm). A mixed solution of acetonitrile and dichloromethane at various volume ratios was used as eluent; the first band could be eluted by this mixed eluent at 1:9 ratio and the second and third bands eluted by the mixed eluent at 3:7. It was impossible, however, to obtain the compounds of these bands because of the too low concentration. Of the eleven bands separated by increasing the dichloromethane contained in the eluent only three isomers corresponding to elution bands 4, 7 and 9 could be isolated. A monomeric complex [Co(sal)(sal$_2$tn)]·H$_2$O was obtained from the fourth elution band with a yield of 59.0 mg; it was shown to be identical with the green form complex **Ib** described above on the basis of IR, UV–Vis and ^{1}H NMR spectra. The seventh band gave [(sal$_2$tn)Co(μ-sal$_2$tn)Co(sal$_2$tn)]·0.5H$_2$O with a yield of 133.0 mg. *Anal.* Found: C, 63.20; H, 5.19; N, 8.29. Calc. for [(sal$_2$tn)Co(μ-sal$_2$tn)Co(sal$_2$tn)]·0.5H$_2$O: C, 63.28; H, 5.11; N, 8.68%. Finally the ninth band gave [(sal$_2$tn)Co(μ-sal$_2$tn)Co(sal$_2$tn)]·2H$_2$O with a yield of 22.6 mg. *Anal.* Found: C, 61.53; H, 4.94; N, 8.28. Calc. for [(sal$_2$tn)Co(μ-sal$_2$tn)Co(sal$_2$tn)]·2H$_2$O: C, 61.56; H, 5.28; N, 8.45%.

Measurements

^{1}H NMR spectra were obtained on Jeol, JNM-MH 100 (at 100 MHz), using deuterochloroform or deuterodichloromethane as the solvent, and the chemical shifts were measured relative to tetramethylsilane.

Infrared spectra were obtained on a Jasco, A302 Spectrophotometer by using KBr disc technique. Electronic specta and reflection spectra were obtained with a Hitachi, Model 200-10 Spectrophotometer; visible and ultraviolet spectra were studied in chloroform, dichloromethane and methanol solutions, and the diffuse reflection spectra in a solid state were obtained by the same instrument equipped with a standard Hitachi reflection attachment.

Differential thermal analysis and thermal gravimetry (TG–DTA) were carried out on samples heated at a rate of 5 °C min^{-1} in the air with a Rigaku-Denki Thermoflex, standard type, differential thermal analyzer.

X-ray Data Collection

The complex crystallizes in rectangular prisms. Although powder samples and very thin crystals appear green, the bulky part of the single crystals appeared red–brown under transmitted light. The size of the specimen employed for data collection was 0.25 × 0.30 × 0.46 mm. Oscillation and

Weissenberg photographs gave Laue symmetry, space group, and approximate unit cell dimensions. The unit-cell dimensions were refined by the least-squares analysis of the θ values of 39 reflections.

Crystal data: [Co(sal)(7,7′-Me-sal$_2$tn)], $C_{26}H_{25}O_4N_2Co$, M.W. = 488.4, monoclinic, a = 32.122(13), b = 9.970(2), c = 14.009(3) Å, β = 106.76(3)°, U = 4296.0(21), F(000) = 2032, D_m = 1.49 g cm^{-3}, D_c = 1.51, Z = 8, space group $C2/c$, μ(Mo Kα) = 27.3 cm^{-1}, λ(Mo Kα) = 0.7107 Å. The intensity data ($2\theta \leqslant 50°$) were collected at room temperature by the use of a Philips PW1100 diffractometer. The ω scan mode was employed. The scan range was 0.9°, and the scan speed, 0.033° s^{-1}. The background was counted for half of the scan time at each side of the scan range. During the data collection, the intensities of three standard reflections were monitored every 3 h in order to check the orientation and stability of the crystal. No appreciable decay was observed. A total of 2398 reflections having $F_o{}^2 \geqslant 3\sigma(F_o{}^2)$ were considered as observed. The intensities were corrected for Lorentz-polarization effects [7] but not for absorption.

Structure Solution and Refinement

The cobalt atom was located from a Patterson synthesis. The other non-hydrogen atom positions were obtained from successive difference-Fourier syntheses. The block-diagonal least-squares refinement with anisotropic temperature factors for all the non-hydrogen atoms gave R = 0.041 and R' = $[\Sigma w\Delta F^2/\Sigma wF_o]^{1/2}$ = 0.066. The function minimized was $\Sigma w(F_o - |F_c|)^2$, where $w = 1/(\sigma^2(F_o) + 0.008F_o{}^2)$ was used. All hydrogen atoms were found in difference Fourier maps, but their coordinates other than those of methyl groups were calculated (C–H = 1.0 Å). In the final cycles of the refinement the hydrogen atoms were included with a common isotropic temperature factor of B = 5.0 Å^2. Their parameters were not refined.

In the final cycle of the refinement all the parameter shifts were less than 0.4σ. The atomic scattering factors for Co, O, N, and C atoms were taken from ref. 8, with correction for $\Delta f'$ for the Co atom. The final difference Fourier map was featureless and showed no peaks greater than 0.2 e Å^{-3}. The atomic coordinates are given in Table I. The computer programs used in the calculations were local versions of UNICS [9]. Figure 1 was drawn by the use of ORTEP [10]. The calculations were performed on a FACOM 230-60 computer at Osaka City University.

TABLE I. Fractional Coordinates and Temperature Factors for β_2-[Co(sal)(7,7′-Me-sal$_2$tn)] [a]

Atom	x	y	z	$U_{eq}{}^a$ or U
Co	0.14294(2)	0.4329(1)	0.12918(4)	0.0326(2)
O(1)	0.1885(1)	0.5154(3)	0.0901(2)	0.037(1)
O(2)	0.1235(1)	0.6020(3)	0.1566(2)	0.043(1)
O(3)	0.0957(1)	0.3511(3)	0.1641(2)	0.042(1)
O(4)	0.1799(1)	0.4380(3)	0.2651(2)	0.041(1)
N(1)	0.1653(1)	0.2588(3)	0.1054(2)	0.035(1)
N(2)	0.1069(1)	0.4365(3)	−0.0064(2)	0.035(1)
C(1)	0.2288(1)	0.4712(4)	0.1321(3)	0.037(1)
C(2)	0.2631(1)	0.5639(5)	0.1505(3)	0.044(2)
C(3)	0.3053(1)	0.5242(5)	0.1976(4)	0.049(2)
C(4)	0.3146(1)	0.3928(5)	0.2292(4)	0.050(2)
C(5)	0.2824(1)	0.2986(5)	0.2061(4)	0.048(2)
C(6)	0.2391(1)	0.3339(4)	0.1553(3)	0.038(1)
C(7)	0.2057(1)	0.2317(4)	0.1177(3)	0.039(2)
C(8)	0.1313(1)	0.1657(4)	0.0501(4)	0.045(2)
C(9)	0.1175(2)	0.2060(4)	−0.0612(3)	0.045(2)
C(10)	0.1239(1)	0.3558(5)	−0.0745(3)	0.044(2)
C(11)	0.0699(1)	0.5003(4)	−0.0377(3)	0.037(1)
C(12)	0.0560(1)	0.6011(4)	0.0225(3)	0.037(1)
C(13)	0.0159(1)	0.6656(5)	−0.0151(3)	0.045(2)
C(14)	0.0031(1)	0.7730(5)	0.0305(4)	0.055(2)
C(15)	0.0315(1)	0.8206(5)	0.1196(4)	0.052(2)
C(16)	0.0705(1)	0.7597(5)	0.1604(3)	0.043(2)
C(17)	0.0843(1)	0.6485(4)	0.1141(3)	0.036(1)
C(18)	0.2208(2)	0.0988(5)	0.0865(4)	0.054(2)
C(19)	0.0412(2)	0.4785(5)	−0.1432(4)	0.053(2)
C(20)	0.0991(1)	0.2881(4)	0.2474(3)	0.038(1)
C(21)	0.0661(2)	0.1975(5)	0.2528(4)	0.049(2)
C(22)	0.0672(2)	0.1349(5)	0.3398(4)	0.054(2)
C(23)	0.1005(2)	0.1587(5)	0.4279(4)	0.055(2)
C(24)	0.1335(2)	0.2428(5)	0.4267(3)	0.049(2)
C(25)	0.1341(1)	0.3076(4)	0.3363(3)	0.042(2)
C(26)	0.1708(1)	0.3865(4)	0.3383(3)	0.039(1)

[a] e.s.d.s given in parentheses. [b] $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij}a^*{}_i a^*{}_j a_i a_j$.

Results and Discussion

Preparation

Although all of the cobalt(III) complexes obtained are insoluble in perfectly non-polar solvents such as hydrocarbons of carbon tetrachloride, they are somewhat soluble in methanol, ethanol, acetone, and acetonitrile, and very soluble in dichloromethane and chloroform. Two sorts of isomers, a brown form suffixed **a** and a green form suffixed b, were obtained for complexes, **I**, **IV**, and **VII**. The fact that both forms of each series give green solutions of the same absorption and ^{1}H NMR spectra in dichloromethane or chloroform and that recrystallization from such a solution invariably gives the green form suggests that the green form is the stable type in each series. Although only the brown form was prepared for **II** or **III** as **IIa** or **IIIa** in the experiment, the stable type is also thought to be a green form because the brown form gave a green solution in chloroform or dichloromethane, and it does not seem difficult to obtain the green form complex **IIb** or **IIIb** from such a solution. On the other hand, only the green forms could be obtained in the case of complexes **V**, **VI**, **VIII**, all of which contained Schiff bases derived

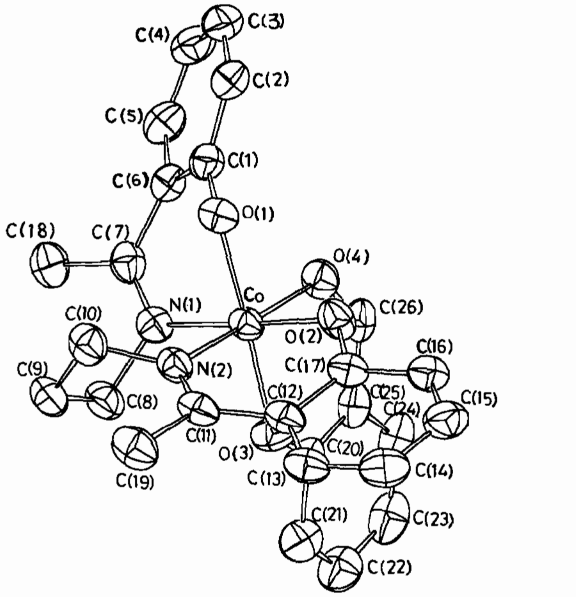
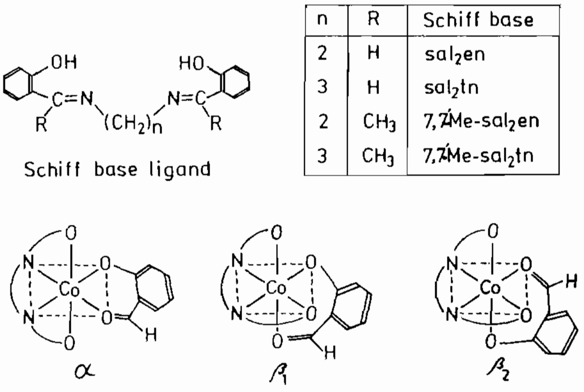


Fig. 1. Perspective views of the complex molecules, showing the atomic numbering. The thermal ellipsoid was drawn at the 50% probability level.



n	R	Schiff base
2	H	sal₂en
3	H	sal₂tn
2	CH₃	7,7'Me-sal₂en
3	CH₃	7,7'Me-sal₂tn

Fig. 2. The Schiff base and the geometric configurations of the [Co(sal)(Schiff base)] complex.

from *o*-hydroxyacetophenone. Each isomeric pair showed different IR spectra, visible spectra of the diffuse reflection in solid state and different TG–DTA curves.

Structure of the Complex

Three isomers, α, β_1, and β_2 are conceivable for each series of the mixed-ligand complexes, as shown in Fig. 2. As it has been very difficult to determine the steric configuration of the isomers from spectroscopic data only, an X-ray crystal analysis of complex **Vb** was undertaken. Figure 1 picks up the perspective view of the complex molecule. The bond lengths, bond angles, and torsion angles are listed in Table II. The coordination around the cobalt atom is an octahedral N_2O_4 structure. The quadridentate ligand 7,7'-Me-sal₂tn is of *cis*-β_2 configu-

TABLE II. Bond Distances, Bond Angles, Torsion Angles and Conformational Analysis of β_2-[Co(sal)(7,7'-Me-sal₂tn)][a]

	X-ray	Conformational analysis
Bond lengths (*l* (Å))		
Co–O(1)	1.894(3)	1.844
Co–O(2)	1.876(3)	1.883
Co–O(3)	1.907(3)	1.918
Co–O(4)	1.933(3)	1.941
Co–N(1)	1.943(3)	1.953
Co–N(2)	1.919(3)	1.933
O(1)–C(1)	1.331(5)	1.316
O(2)–C(17)	1.310(5)	1.316
O(3)–C(20)	1.301(5)	1.315
O(4)–C(26)	1.254(6)	1.246
N(1)–C(7)	1.287(6)	1.310
N(1)–C(8)	1.472(5)	1.498
N(2)–C(10)	1.469(6)	1.497
N(2)–C(11)	1.305(5)	1.307
C(1)–C(6)	1.424(6)	1.424
C(6)–C(7)	1.464(6)	1.463
C(7)–C(18)	1.518(7)	1.534
C(8)–C(9)	1.546(7)	1.545
C(9)–C(10)	1.427(7)	1.544
C(11)–C(12)	1.462(6)	1.467
C(11)–C(19)	1.515(6)	1.534
C(12)–C(17)	1.422(5)	1.426
C(20)–C(25)	1.429(5)	1.419
C(25)–C(26)	1.413(6)	1.435
Bond angles (*ϕ* (°))		
N(1)–Co–N(2)	89.7(1)	89.96
O(2)–Co–N(2)	92.5(1)	89.96
O(3)–Co–O(4)	93.9(1)	90.13
Co–O(1)–C(1)	117.5(3)	119.61
O(1)–C(1)–C(6)	123.6(4)	122.56
C(1)–C(6)–C(7)	119.2(3)	119.95
C(6)–C(7)–N(1)	120.6(4)	122.14
Co–N(1)–C(7)	124.9(3)	121.55
Co–N(1)–C(8)	113.5(3)	113.30
N(1)–C(8)–C(9)	108.7(4)	108.75
C(8)–C(9)–C(10)	111.6(4)	110.95
C(9)–C(10)–N(2)	111.6(4)	112.67
Co–N(2)–C(10)	113.7(2)	112.48
Co–N(2)–C(11)	124.9(3)	123.37
N(2)–C(11)–C(12)	122.7(3)	122.53
C(11)–C(12)–C(17)	121.8(4)	121.30
C(12)–C(17)–O(2)	124.9(4)	123.44
Co–O(2)–C(17)	123.9(3)	121.36
Co–O(3)–C(20)	124.6(2)	128.68
O(3)–C(20)–C(25)	124.0(4)	123.92
C(20)–C(25)–C(26)	122.3(4)	120.05
C(25)–C(26)–O(4)	127.0(4)	127.68
Co–O(4)–C(26)	125.0(3)	127.63
N(1)–C(7)–C(18)	122.5(4)	120.44
C(6)–C(7)–C(18)	116.6(4)	117.41
N(2)–C(11)–C(19)	119.7(4)	121.62
C(12)–C(11)–C(19)	117.4(4)	115.85
C(7)–N(1)–C(8)	120.3(4)	121.55
C(10)–N(2)–C(11)	121.4(3)	123.08

(continued)

TABLE II. *(continued)*

	X-ray	Conformational analysis
Torsion angles (τ (°)) about		
N(1)–C(8)	76.7(4)	77.48
C(8)–C(9)	28.1(6)	28.58
C(9)–C(10)	46.5(6)	46.59
N(2)–C(10)	74.8(4)	74.54

^{a}e.s.d.s are given in parentheses.

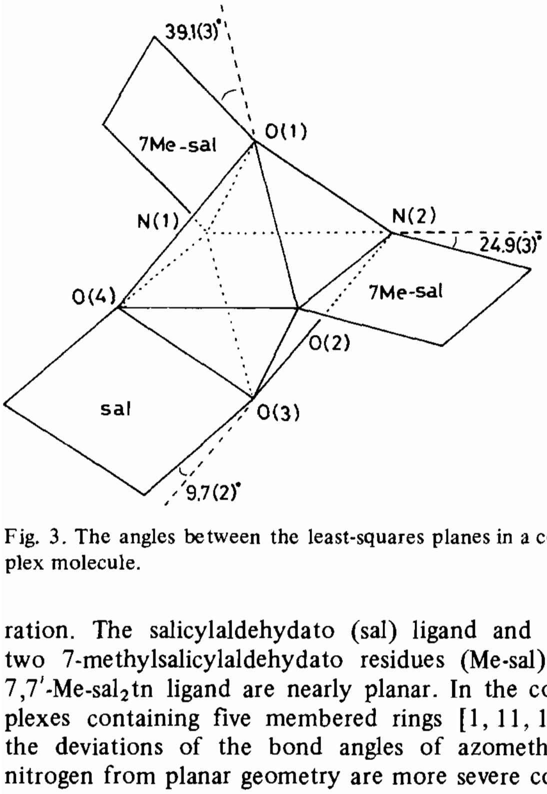


Fig. 3. The angles between the least-squares planes in a complex molecule.

ration. The salicylaldehydato (sal) ligand and the two 7-methylsalicylaldehydato residues (Me-sal) in 7,7′-Me-sal$_2$tn ligand are nearly planar. In the complexes containing five membered rings [1, 11, 12], the deviations of the bond angles of azomethine nitrogen from planar geometry are more severe comparing with those in the complexes containing six or seven [13] membered ring. This tendency can also be seen markedly in the conformational analyses (*vide post*) for [Co(sal)(sal$_2$en)] (VII) and [Co(sal)(7,7′-Me-sal$_2$en)] (VIII) complexes, the α isomers of which have extraordinary high strain energies.

Figure 3 gives the angles between the planes passing through sal, Me-sal(1), and Me-sal(2) groups the three equatorial planes of the octahedron around the cobalt atom. The deviations of these groups from the equatorial planes are larger than those in [Co(sal$_2$en)(acac)] [1], but are comparable with those in $(-)_{435}$-Λ_{RS}-β_2[Co(α-Me-sal$_2$en)(N-Bz-L-ala)] [11]. The central six membered ring in 7,7′-Me-sal$_2$tn ligand is of the skew-boat conformation. The bond angles and torsion angles in the ring indicate that the skew-boat is less flattened than that found in the chromium(III) complex [14].

The Co–O(4)(aldehyde) bond is *ca.* 0.03 Å longer than the Co–O(3)(phenol) bond in the Co-sal group, probably suggesting the weakness of the former. This may be related with the fact that the known examples of aldehyde complexes are very few; the present analysis is the first case in which the aldehyde coordination has been established.

The crystal consists of discrete [Co(sal)(7,7′-Me-sal$_2$tn)] molecules. All contacts are of the van der Waals type and intermolecular contacts are normal. The shortest distance is C(12)–C(23) (x, $1-y$, $-\frac{1}{2}+z$) 3.259(7) Å.

Conformational Analysis

Since it proved difficult to obtain good single crystals of compounds other than **Vb** especially brown isomers, the structure relationship was further examined by means of conformational analysis. Such analysis was considered to be of value from the preparative point of view also, since it often occurs in the field of coordination chemistry that only limited number of isomers can actually be prepared.

Empirical force field (strain energy minimization) calculations were carried out by employing a modification of the MM2 program by Allinger and co-workers [15]. The bond-stretching force constant of 1.75 mdyn/Å was used for all the coordination bonds [16]. The other force constants and parameters were adopted or estimated from those of the MM2 program and the literatures [16–18].

In the course of the analysis, it proved difficult to determine which isomer has the lower energy, because the energy differences are very small. The authors, therefore, decided to introduce a new factor which has not been considered in the conventional conformational analysis: the effect of intramolecular electrostatic interactions due to charge localization. In such a treatment all electric charges of a complex molecule were assumed to be distributed to the cobalt atom (positive) and lone paired electrons (negative) on the phenolato oxygens. Some equilibrium bond distances and angles were adjusted for the structure of β_2-[Co(sal)(7,7′-Me-sal$_2$tn)] (**Vb**) to fit better to that obtained by the X-ray method.

The last column in Table II gives the molecular-geometry values obtained for the case where the electric charges of six lone pairs of electrons are −0.2. The electric charges were changed in the range of −0.1 to −0.25 in energy minimization. In Fig. 4, the calculated strain energies of the energy-minimized structures are summarized for the three possible existent geometrical isomers (α, β_1 and β_2) of the four salicylaldehydato complexes (**I**, **V**, **VII** and **VIII**). It can be seen that the formation of the α isomer is difficult or impossible. This is consistent with the experimental results that the α isomer could not be obtained in all the cases. The relative

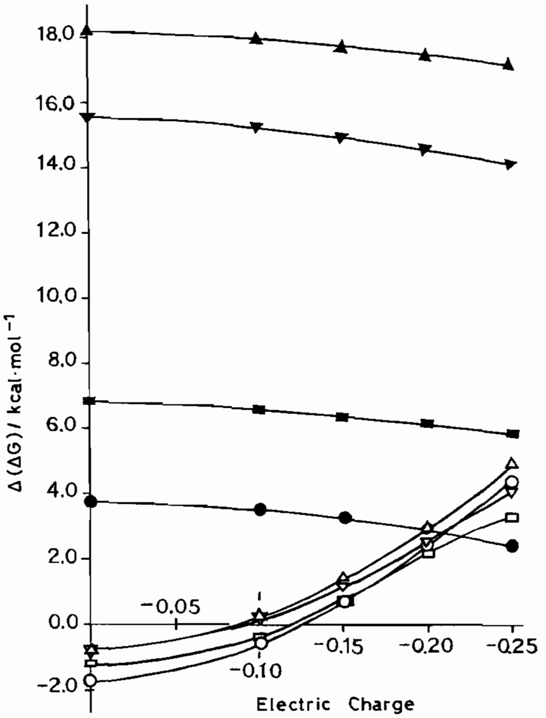


Fig. 4. The relative strain energies *vs.* the electric charges of the lone-paired electrons on the phenolato oxygens. The β_2 isomer is used as a standard. The solid symbols, ▲, ▼, ■, and ●, are for the α isomers of VII, VIII, I, and V, respectively; the corresponding open symbols are the the β_1 isomers.

stability of the β_1 to the β_2 isomer is similar for the four complexes. The electric charges of lone-paired electrons in the cobalt(III) complexes should be less than the value −0.3, which is estimated for ordinary organic compounds from the bond–dipole moment (MM2), because the charge of a cobalt atom bonded to oxygens is much higher than that of a proton. The results of strain energies calculated with the electric charge of −0.2, for example, are compatible with the isolation of only the β_2 isomers (**Vb** and **VIIIb**) for the **V** and **VIII** complexes, and the fact that although the β_1 isomers were also isolated in the case of **I** and **VII**, they are isomerized easily to the β_2 form in chloroform or dichloromethane solutions. The isolation of metastable β_1 forms of **I** and **VII** might be due to its easier formation from the starting Co(II) complex from the kinetic viewpoint and the comparatively low solubility in methanol. The inclusion of intramolecular electrostatic interactions in the conformational analysis as attempted above is expected to bring about refinements in a wider range of similar systems, as well.

^1H *NMR Spectra*

^{1}H NMR spectra of the complexes are shown in Figs. 5 and 6, and the data of the chemical shifts are listed in Table III. In conformity with the conclusion from X-ray and conformational analysis, most of the spectral feature seems to be explicable on the assumption that all the complexes exist in the β_2 form in solution.

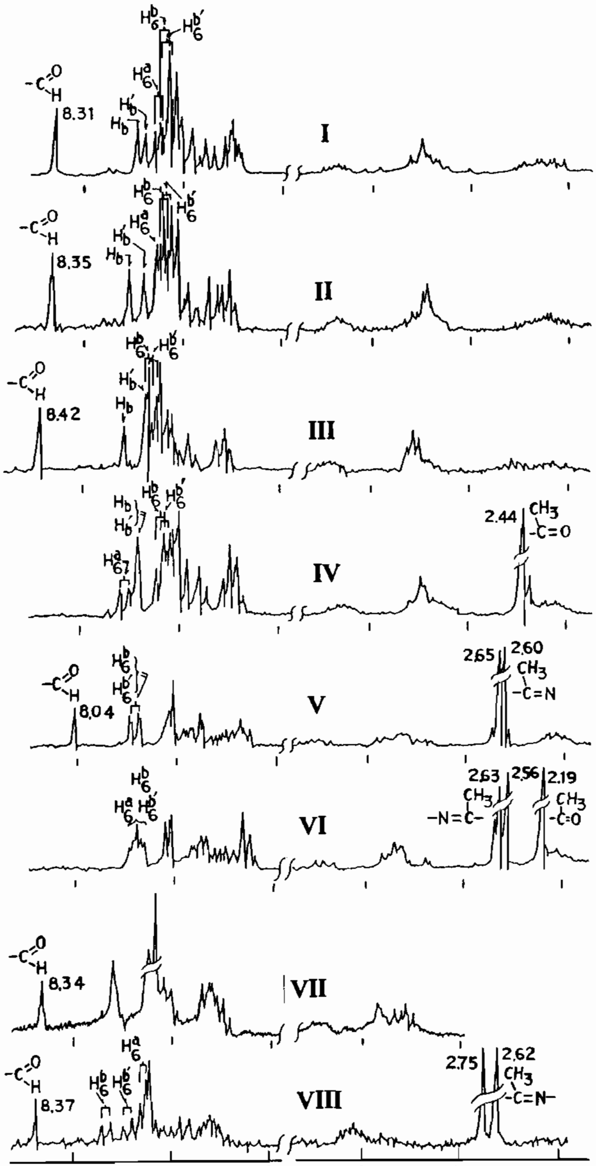


Fig. 5. ^{1}H NMR spectra of the complexes (from I to VIII) in CD_2Cl_2.

The methine proton of the CHO group in the complexes can be assigned to a singlet peak in a low magnetic field region from 8.04 to 8.42 ppm. In complexes **IV** and **VI** which have $COCH_3$ instead of CHO, methyl protons resonate at 2.44 and 2.19 ppm, respectively.

The two methine protons of the −CH=N− groups of the complexes **I**–**IV** and **VII** in a deuterodichloromethane resonanced at Hb and Hb′. On the other

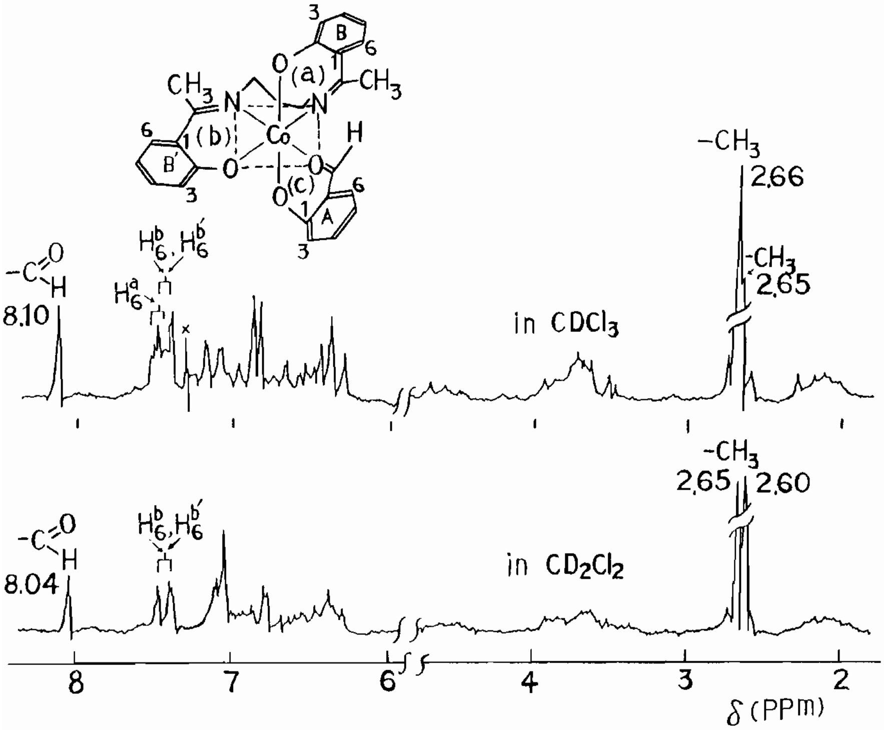
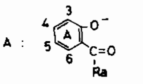
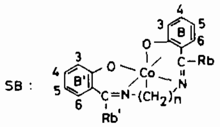


Fig. 6. ^1H NMR spectra of the β_2-[Co(sal)(7,7'-Me-sal$_2$tn)] in $CDCl_3$ and CD_2Cl_2

TABLE III. ^1H NMR Spectra of the Complexes in CD_2Cl_2

[Co(A)(SB)p]		A: 				SB: 						
Complex	$-(CH_2)_n-$		Ra	H_3^a	H_6^a		Rb'	Rb	$H_3^{b'}$	H_3^b	$H_6^{b'}$	H_6^b
I	$n = 3$	H	8.30	6.54	7.26	H	7.39	7.47	6.41	6.45	7.18	7.19
II	$n = 3$	H	8.35	6.73	7.30	H	7.42	7.56	6.53	6.57	7.23	7.26
III	$n = 3$	H	8.42		7.33	H	7.36	7.57	6.53	6.58	7.28	7.32
IV	$n = 3$	CH_3	2.44	6.52	7.56	H	7.42	7.42	6.39	6.44	7.16	7.19
V	$n = 3$	H	8.04	6.32	7.10	CH_3	2.60	2.65	~6.5~		7.44	7.44
VI	$n = 3$	CH_3	2.19	6.35	7.42	CH_3	2.56	2.63	6.27	6.21	7.34	7.37
VIII	$n = 2$	H	8.37	~6.4~	7.35	CH_3	2.62	2.75	~6.4~		7.44	7.67

hand, in the complexes **Vb**, **VIb** and **VIIIb**, resonance peaks due to the methyl protons of the 7,7'-Me-sal$_2$tn or 7,7'-Me-sal$_2$en appear in the high-field region from 2.56 to 2.75 ppm. It may be expected that in the β configuration the methine proton in the chelate ring of the Schiff base which makes a smaller angle to the coordination plane resonates at a higher magnetic field (Rb', Table III) as compared with that (Rb, Table III) in the chelate ring which makes a larger angle to the coordination plane because of the higher steric strain at the –CH=N– part in the former. The same thing might be said about the methyl protons of the $-C(CH_3)=N-$ parts of the two chelate rings [19, 20]. It seems to be due to a solvent effect that the ^1H NMR spectrum of the **Vb** in deuterochloroform differs a little from the one in deuterodichloromethane as shown in Fig. 6.

Reflection and Solution Absorption Spectra

Reflection spectra of powder samples are given in Fig. 7, and solution absorption spectra are given in Figs. 8 and 9. The results show that whereas brown and green isomers in each series give distinctly different diffuse reflection spectra, each two isomers give completely the same absorption spectrum when

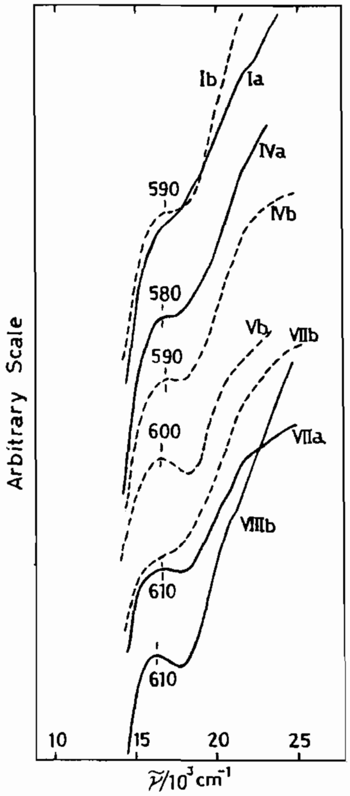


Fig. 7. Reflection spectra of the complexes **Ia** and **Ib**, **IVa** and **IVb**, **Vb**, **VIIa** and **VIIb**, and **VIIIb**.

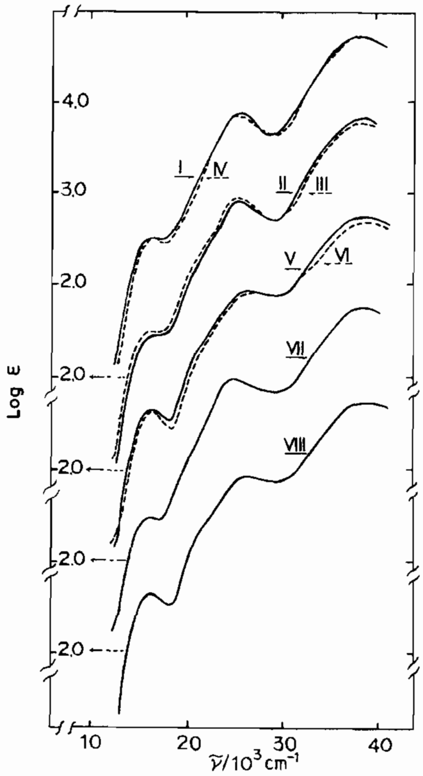


Fig. 8. Absorption spectra of the complexes (from **I** to **VIII**) in CH_2Cl_2.

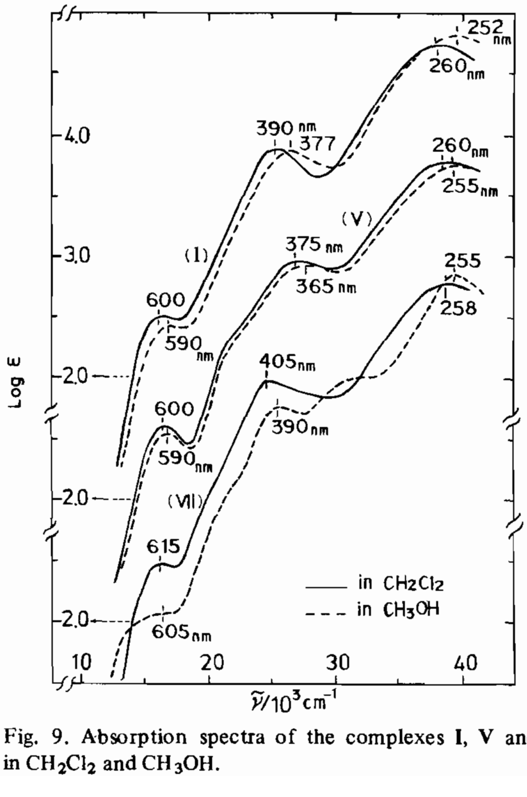


Fig. 9. Absorption spectra of the complexes **I**, **V** and **VII** in CH_2Cl_2 and CH_3OH.

dissolved in the same solvent. This indicates that the isomerization of the brown forms to the green forms proceeds very quickly in solution. The resemblances between the spectra of salicylaldehydato complexes and those of the corresponding *o*-hydroxyacetophenonato complexes seem to suggest that they both have the same configuration (**I–IV**, **V–VI**, Fig. 8).

In methanol solutions, the absorption peaks of **Ia** and **Vb** appear at shorter wave lengths as compared with those in dichloromethane, as shown in Fig. 9. Furthermore, in the absorption spectrum of **VIIa** in methanol, a new peak appears at 31 500 cm^{-1} and the first band is broadened considerably.

TG–DTA

TG–DTA curves of the complexes in air are given in Fig. 10. In the complex **VIIa**, weight loss from room temperature to about 130 °C is found to be due to dehydration of water of crystallization and an exothermic peak in the DTA curve at 179 °C and a large weight loss in the TG curve around this temperature seems to be due to partial cleavage and elimination of salicylaldehyde. An analogous exothermic peak in the DTA curve for the **VIIb** complex appears at 199 °C, which is at a higher temperature than that for **VIIa**, suggesting that

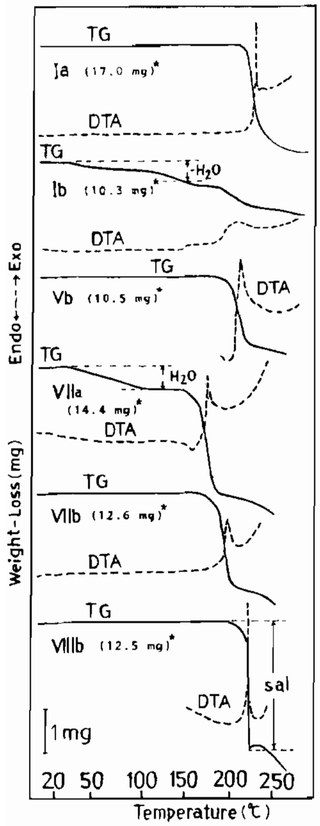


Fig. 10. Thermal curves for the complex [Co(sal)(Schiff base)] (**Ia**, **Ib**, **Vb**, **VIIa**, **VIIb** and **VIIIb**). *Weight. taken (mg).

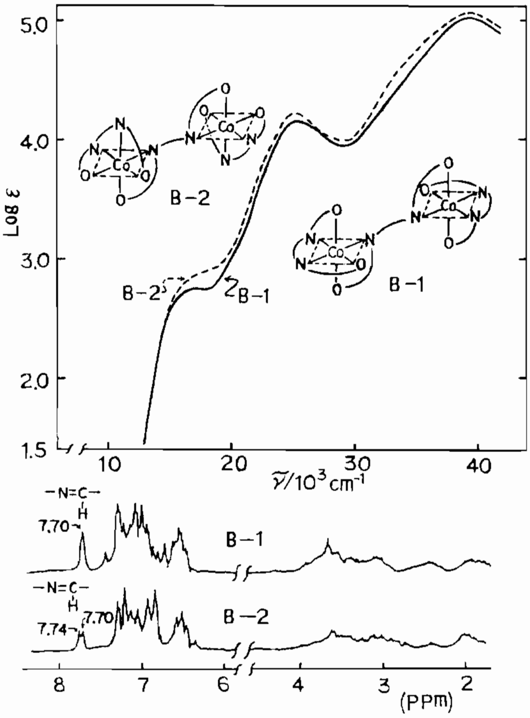


Fig. 11. Absorption spectra (top) and ^1H NMR spectra (bottom) of the binuclear complexes (**B-1** and **B-2**) in CH_2Cl_2 and CD_2Cl_2, respectively.

VIIb is more stable on heating than **VIIa** in the solid state. Thermal decomposition of **Ia** having no water of crystallization begins to take place at about 220 °C and an exothermic peak in the DTA curve appears at 234 °C, while **Ib** loses one molecule of water of crystallization in two stages from near room temperature to about 150 °C and then decomposes slowly near 187 °C with a weight loss. In the **VIIIb** complex, weight loss corresponding to one molecule of salicylaldehyde takes place at about 225 °C and an exothermic peak in the DTA curve appears at this temperature. **Vb** begins to decompose at 190 °C and the exothermic peak in the DTA curve appears at about 216 °C, which is lower than that for **VIIIb**.

Infrared Spectra

The data of the infrared spectra of the complexes are summarized in Table IV. The weak peaks in the region from 3010 to 3080 cm^{-1} may be assigned to ν(C–H) of the phenylene ring, and those in the region from 2850 to 2980 cm^{-1}, to ν(C–H) of aldehyde and methylene groups. Since ν(C=O) bands of the free aromatic aldehyde near 1700 cm^{-1} shift to the lower energy region near 1600 cm^{-1} by the coordination of the C=O group to the metal ion, the ν(C=C) and ν(C=O) of all the complexes given in Table IV were observed very close to each other because the ν(C=C) bands due to the phenylene ring also appeared around 1600 cm^{-1}. The bands in the region from 1510 to 1530 cm^{-1} are assigned to the skeletal vibration of the phenol groups.

Column Chromatography, Absorption Spectra and ^1H NMR Spectra

In a silica-gel column chromatography of the solution obtained by air-oxidation of [Co^{II}(sal$_2$tn)] in dichloromethane, two sorts of isomers of the binuclear complex [(sal$_2$tn)Co(μ-sal$_2$tn)Co(sal$_2$tn)] were isolated, which are labelled **B-1** (seventh band) and **B-2** (ninth band). It was impossible to isolate the complex of the eighth elution band because the concentration was too low.

As has been already described, conformational analysis of the mixed-ligand complex [Co(sal)(sal$_2$-tn)] indicated the superiority of the β form configuration in their stability. If the coordination of the terminal sal$_2$tn to both Co(III) ions of the binuclear complex is also in the β form, the following three geometrical isomers are conceivable in the order of increasing dipole moment: *mer*(O),*mer*(O)-[Co(N_3-O_3)-Cp(N_3O_3)]; *mer*(O),*fac*(O)-[Co(N_3O_3)-Co(N_3-O_3)]; *fac*(O),*fac*(O)-[Co(N_3O_3)-Co(N_3O_3)]. The order of elution is also expected to be as above, if it is assumed that the adsorbing ability increases

TABLE IV. IR Data of Complexes (cm^{-1})

Complex	ν(C–H) (C_6H_6)	ν(C–H) CHO –CH_2–	ν(C=O) ν(C=C)	ν(C–O) (phenol)	ν(C–O) (phenol) δ(C–H) (wag.) CH_3 (rocking)		δ(C–H)(C_6H_6, out-of-plane wag.)
Ia	3050w 3010w	2940w 2870w	1610vs 1595vs	1535s 1515s	1210m 1190m	1150m 1140m 1125m	755vs, 735w, 730w
Ib	3050w 3020w	2980vw 2930w	1610vs 1595vs	1535s 1520s	1210m 1195m	1145m 1125m	755s, 735m
IIa	3060vw	2950w 2880vw	1620s 1600s	1538m 1510s	1238w 1204m	1160s 1150sh 1130m	770m, 760s, 742s
IIIa	3050w	2920w 2870vw	1620vs 1605vs 1590vs	1533m 1505m	1210m 1197s	1153s 1145s 1124m 1118m	770s, 755s, 750sh 730m, 710m
IVa	3045w 3015vw	2980vw 2930w 2860vs	1620vs 1605vs 1590vs 1583vs	1533s 1520s	1210 1195m 1250w 1230s	1150m 1140m 1125m	750vs, 735m 735m
IVb	3045w	2960sh 2922w 2860w	1620vs 1605vs 1590vs 1583vs	1525m 1522s	1200sh 1250w 1230s	1145m 1125m	750s, 735sh
Vb	3070w 3040vw 3010w	2980vw 2920w 2870vw 2850vw	1610vs 1605vs 1590vs	1535s 1523s	1210m 1190m 1255m 1245sh 1234m	1127m 1135m 1145m	765s, 743s, 720m
VIa	3075w 3025w	2975w 2925w 2860w	-1600-sh 1595vs	1525s 1510sh	1210s 1255s	1158s 1135vs 1230vs	770, 760vs, 745vs 722s
VIIa	3040w 3020vw	2940w	1635s 1610vs 1590vs	1530sh 1515s	1210m 1195m	1145s 1125m	755s, 730m
VIIb	3045w 3010w	2930w	1635sh 1610vs 1595vs	1530sh	1205sh	1145m	753s
VIIIb	3050w 3015w	2960w 2880w	1625sh 1610 1590$^{\text{bro}}$	1535sh 1520s	1200m 1190m 1258m 1235m	1160m 1143s 1125m	770s, 762s, 750s 725m

with increasing dipole moment. This suggests assignment of **B-1** and **B-2** to *mer*(O),*mer*(O) and *fac*(O),*fac*(O) isomers, respectively, and the minor component in the eighth elution band (appearing between **B-1** and **B-2**, but not isolated) to the *mer*(O),*fac*(O) isomer. A closely related binuclear complex, [Co(3-MeO-salen)$_3$,2H_2O,2MeSO] which was isolated by Calligaris *et al.* was shown by these authors to have the *mer*(O),*mer*(O) structure by X-ray crystallography [21].

The electronic absorption and ^{1}H NMR spectra of the binuclear complexes **B-1** and **B-2** are shown in Fig. 11. That the absorption spectra of **B-1** and **B-2** are very similar to the reflection spectra of **Ib** (β_2) and **Ia** (β_1), respectively, of the monomeric mixed ligand complex [Co(sal)(sal$_2$tn)] in the visible region, may be in line with the above assignment of **B-1** and **B-2** to *mer*(O),*mer*(O) and *fac*(O),*fac*(O) forms as inferred from the elution order on the chromatogram.

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