Communications to the Editor

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β_1 and β_2-Isomers of Salicylato(triethylenetetramine)cobalt(III) Complex

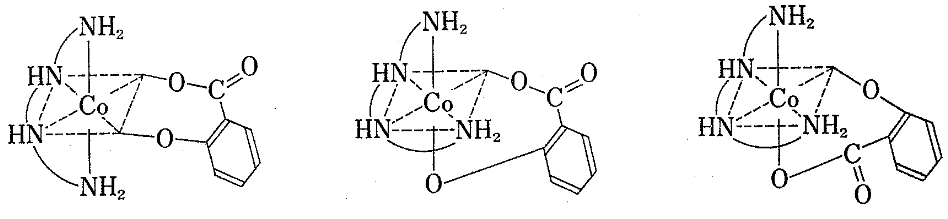
β_1- and β_2-isomers of salicylato(triethylenetetramine)cobalt(III) chloride monohydrate have been isolated and characterized by analytical and spectroscopic methods.

The ^{13}C–NMR spectra of those complexes have shown two different configurations (β_1 and β_2) of the complex.

Keywords——salicylic acid; β_1 and β_2-isomers; triethylenetetramine; cobalt complex; ^{1}H-NMR; ^{13}C-NMR

Although studies on the stereochemistry of [Co(trien)(amino-acidato)]$^{2+}$ complex (trien=triethylenetetramine, amino-acidato=glycinato, sarcosinato…) were reported by some authors,[1,2] no report has appeared on the configuration of cobalt(trien) complex which is chelated by two oxygen atoms such as salicylic acid as far as the present authors know.

The β-salicylato(triethylenetetramine)cobalt(III) chloride monohydrate has been obtained from salicylic acid and β-[Co(trien)Cl$_2$]Cl by Morgan's method[3] at pH 8—9. Attempts to obtain α-form using α-[Co(trien)Cl$_2$]Cl invariably resulted in the isolation of mixture of β_1 and β_2 forms. The α-form can be thermodynamically unstable[4] at pH 7—8. The separation of its two isomers β_1 and β_2 was attempted by using ion exchange resin.[1,2] On elution with a 0.3 M NaCl solution, the band of the complex split into two. The solution of the first band (**1a**) and of the second band (**1b**) were concentrated in a rotary evaporator and NaCl was removed by filtration. Complexes **1a** and **1b** were recrystallized from water, respectively. *Anal.* Calcd. for $C_{13}H_{24}ClCoN_4O_4$: C, 39.56; H, 6.13; Cl, 8.98; N, 14.19. Found **1a**: C, 39.47; H, 6.07; Cl, 8.76; N, 14.45. **1b**: C, 39.68; H, 6.14; Cl, 9.00; N, 14.39.



α β_1 β_2

Fig. 1. The α, β_1 and β_2 Configuration of Complex 1

Buckingham *et al.* who studied the IR-spectra of β_1, β_2 and α-[Co(trien)gly]$^{2+}$ [2,4] reported that the IR-spectra of β-(trien)cobalt(III) complexes showed at least four strong absorption bands and those of α-(trien)cobalt(III) complexes showed two strong absorption bands in the 990—1100 cm^{-1} region. The IR-spectra of complexes **1a** and **1b** have four strong peaks in this region. The spectrum of **1a** and that of **1b** in this region are close to that of β_1-[Co(trien) gly]$^{2+}$ and to those of β_2-[Co(trien)gly]$^{2+}$, β_2-[Co(trien)sar]$^{2+}$,[4] and β-[Co(trien)Cl$_2$]$^+$ [5] respectively. This indicates that the complexes assume the β-form.

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1) D.A. Buckingham, P.J. Cresswell, R.J. Dellaca, M. Dwyer, G.J. Gainsford, and L.G. Marzilli, *J. Am. Chem. Soc.*, **96**, 1713 (1974).
2) D.A. Buckingham, M. Dwyer, G.J. Gainsford, V. Janson Ho, L.G. Marzilli, Ward T. Robinson, A.M. Sargeson, and K.R. Turnbull, *Inorg. Chem.*, **14**, 1739 (1975).
3) G.T. Morgan and J.D.M. Smith, *J. Chem. Soc.*, **1924**, 1924.
4) L.G. Marzilli and D.A. Buckingham, *Inorg. Chem.*, **6**, 1042 (1967).
5) D.A. Buckingham and D. Jones, *Inorg. Chem.*, **4**, 1387 (1965).

The ^1H–NMR spectra of both **1a** and **1b** showed five peaks of the intensity ratio of 1:1:1:1:2 in 0.1 M D_2SO_4 and in 0.1 M DCl. It was reported by Buckingham that the order of chemical shifts in ppm is $NHR_1R_2 < NH_2R < NH_3$.[4,6] Thus the secondary NH protons of coordinated trien absorb at lower fields than the terminal NH_2 protons. Also in the $[Co(NH_3)_4sal]^+$ ion it has been found that the NH_3 protons in a position *trans* to the coordinated carboxyl oxygen[7] of the salicylato ligand absorb at the highest field. Again in the spectra of *cis* β_2-$[Co(trien)sar]^{2+}$ ions, the NH_2 protons in a position *trans* to the coordinated carboxyl oxygen[4] of the sarcosinato ligand absorb at a higher field than those *cis* to the carboxyl oxygen. As regards **1a** and **1b**, the signal for NH_2 group of complex **1b** is at a higher field than that of **1a**. Therefore the NH_2 group in the complex **1b** is at a position *trans* to the carboxyl oxygen of the salicylato ligand. Thus complex **1b** and **1a** can be assigned to β_2 and β_1, respectively. The observed chemical shifts (in δ) of complex **1a** are 2.39—3.89 (12H, CH_2), 4.50 (2H, NH_2), 5.29 and 6.29 (each 1H, NH), 6.56—7.99 (5H, NH+salicylato) in 0.1 M D_2SO_4, and 2.35—3.72 (12H, CH_2), 4.43 (2H, NH_2), 5.24 and 6.25 (each 1H, NH), 6.49—7.95 ppm (5H, NH+salicylato) in 0.1 M DCl. The chemical shifts of complex **1b** are 2.30—3.80 (12H, CH_2), 4.40 (2H, NH_2), 5.25 and 6.19 (each 1H, NH), 6.50—7.94 (5H, NH+salicylato) in 0.1 M D_2SO_4, 2.31—3.68 (12H, CH_2), 4.31 (2H, NH_2), 5.23 and 6.18 (each 1H, NH), 6.51—7.94 (5H, NH+salicylato) in 0.1 M DCl, and 2.35—3.73 (12H, CH_2), 6.62—7.93 (4H, salicylato) in D_2O and NaOH. Internal DSS was used as standard.

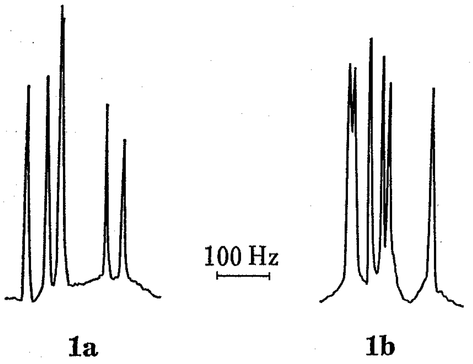
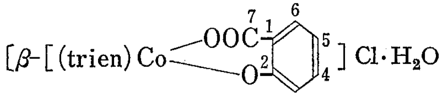


Fig. 2. ^{13}C–NMR{^1H} Spectra of Trien of Complexes **1**



in D_2O

Standard: internal dioxane (δ=67.4 ppm).

The ^{13}C–NMR spectra of complexes **1a** and **1b** were measured in heavy water. There have been observed six signals for trien and seven signals for salicylato ligand in complexes **1a** and **1b**, respectively. The chemical shifts of the salicylato ligand[7] of both complexes agreed with each other: 118.6 (c-1), 167.8 (c-2), 117.4 (c-3), 134.3 (c-4), 124.2 (c-5), 132.4 (c-6), 174.6 (c-7) ppm for complexes **1a** and **1b**. However, those of trien were different, as shown in Figure 2: 43.6, 45.8, 51.8, 52.1, 53.9 and 56.3 for complex **1a** and 42.0, 47.5, 48.3, 49.7, 52.1 and 52.7 ppm for **1b**. Although they are difficult to assign to the individual carbon atoms, they show two different configurations (β_1 and β_2, Fig. 1).

When complexes **1a** and **1b** are treated with 60% nitric acid very deep green solutions are formed. They should contain complexes[8–10] similar to $[CoL_4sal]Cl \cdot H_2O$, (L: NH_3, L_2: en). The equivalent conductance was Λ=93 for complex **1a** and 124 S cm^2 for **1b**. The visible absorption spectra in water showed peaks at 530 mμ (ε=300) for **1a** and at 520 mμ (ε=290) for **1b**. Complex **1b** is diamagnetic, and should be a cobalt(III) complex of low spin type.

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6) D.A. Buckingham, L.J. Durham, and A.M. Sargeson, *Aust. J. Chem.*, **20**, 257 (1967).
7) Y. Yamamoto, Z. Kanda, and E. Toyota, Abstr. No. 3A06, 27th Symposium of Coordination Chemistry of Chemical Society of Japan, Matsumoto, September 1977.
8) Y. Yamamoto, K. Ito, H. Yoneda, and M. Mori, *Bull. Chem. Soc. Jpn.*, **40**, 2580 (1967).
9) Y. Yamamoto, M. Mori, H. Yoneda, S. Misumi, and K. Ito, *Bull. Chem. Soc. Jpn.*, **42**, 984 (1969).
10) Y. Yamamoto, *Bull. Chem. Soc., Jpn.*, **42**, 999 (1969).

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Photochemical Addition of Methanol to Chromones

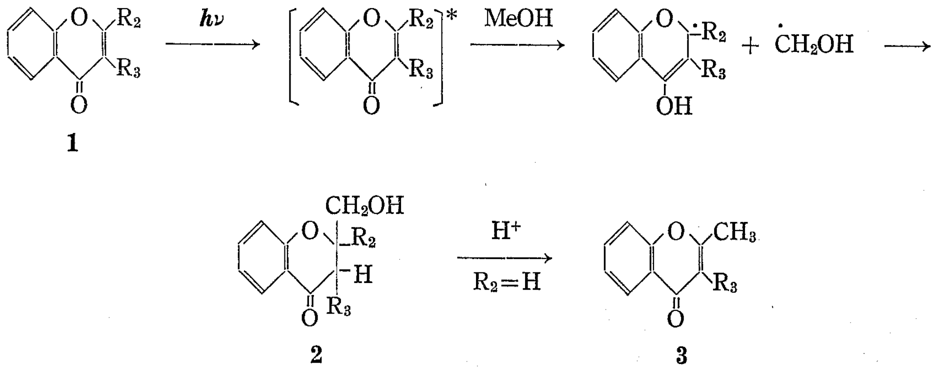
Irradiation of chromones in MeOH–HCl induced the homolytic addition of methanol to the double bond in the pyrone ring to give the 2-hydroxymethylated chromanones.

Keywords——photochemical addition; chromones; 2-hydroxymethylchromanone; 2-methylchromone; n-π^* triplet state

Flavonoids were found in many plants and their photochemical reactions have been studied in detail.[1] In connection with our studies on flavonoids,[2] we have examined the photochemical behavior of chromones in acidic media.

Irradiation of 2-methylchromone (**1a**) in methanol containing 5% hydrochloric acid by 400 W high-pressure mercury lamp (Toshiba H-400 P) with a pyrex filter until all of the starting material had been consumed, resulted in the formation of **2a**, mp 86—87°, in 70% yield. The physical data of **2a** [*m/e* 192 ($M^+=C_{11}H_{12}O_3$); infrared spectrum (IR) ν_{max}^{KBr} cm^{-1}: 3340 (OH), 1680 (C=O); ultraviolet spectrum (UV) λ_{max}^{MeOH} nm (log ε): 223 (2.24), 252 (2.78), 324 (1.40); proton magnetic resonance (PMR) δ ($CDCl_3$): 1.15 (3H, s, 2-CH_3), 2.50 (1H, d, J=16 Hz, 3-CH_2), 3.13 (1H, d, J=16 Hz, 3-CH_2), 3.67 (2H, s, 2-CH_2O), 6.7—7.9 (4H, m, aromatic-H)] indicated it to be 2-hydroxymethyl-2-methylchromanone.

By the irradiation of **1b** under the same condition, 2-hydroxymethyl-2,3-dimethylchromanone (**2b**): [*m/e* 206 ($M^+=C_{12}H_{14}O_3$); IR ν_{max}^{Liquid} cm^{-1}: 3320 (OH), 1680 (C=O); PMR δ ($CDCl_3$): 1.15 (3H, s, 2-CH_3), 1.20 (3H, d, J=7 Hz, 3-CH_3), 3.30 (1H, q, J=7 Hz, 3-CH), 3.70 (2H, s, 2-CH_2O), and 6.7—7.9 (4H, m, aromatic-H)] was obtained as an oil in 70% yield.



	R₂	R₃
a :	CH_3	H
b :	CH_3	CH_3
c :	H	CH_3
d :	H	H

Fig. 1

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1) T. Matsuura, H. Matsushima and H. Sakamoto, *J. Am. Chem. Soc.*, **86**, 6370 (1967); T. Matsuura, T. Takemoto, and R. Nakashima, *Tetrahedron Lett.*, **1971**, 1539; A.C. Waiss, R.E. Ludin, A. Lee, and J. Corse, *J. Am. Chem. Soc.*, **89**, 6213 (1967).

2) M. Komatsu, I. Yokoe, and Y. Shirataki, *Chem. Pharm. Bull.* (Tokyo), **26**, 1274 (1978).