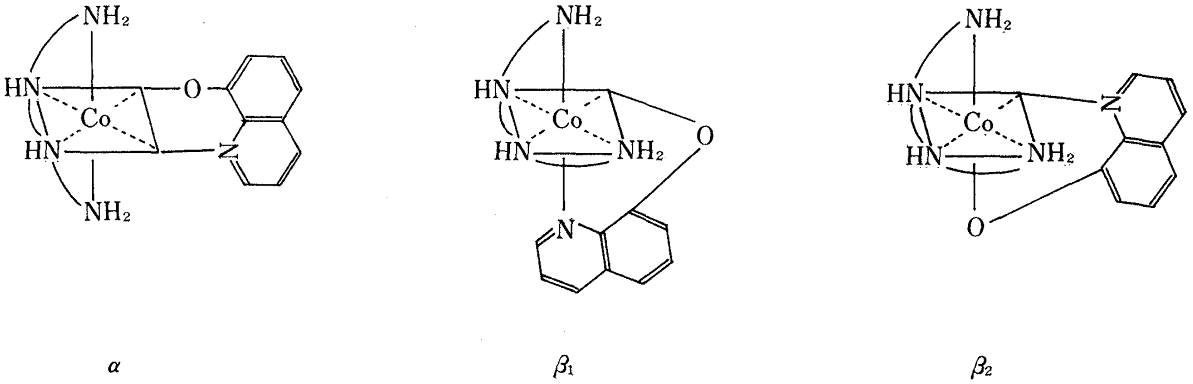
Chem. Pharm. Bull.
28(10)3153—3155(1980)

Isolation of β_1- and β_2-(8-Quinolinolato)(triethylenetetramine)cobalt(III) Complexes

β_1- and β_2-8-Quinolinolato(triethylenetetramine)cobalt(III) chloride dihydrate, β-$[Co(oxine)trien]Cl\cdot 2H_2O$, have been isolated and characterized by analytical and spectroscopic methods.

Keywords——8-quinolinol; β_1- and β_2-isomers; triethylenetetramine; cobalt complex; ^1H-NMR; ^{13}C-NMR

Although preparation of tris(8-quinolinolato)metal complexes,[1] alkyl[2] or bis (8-quinolinolato)dichlorometal complexes[3] has already been reported, amine(8-quinolinolato)metal complex has never been described, because 8-quinolinol has powerful chelating ability with metals.[4] We have now isolated β_1- and β_2-8-quinolinolato(triethylenetetramine)cobalt(III) chloride dihydrate from the reaction mixture of 8-quinolinol, α-dichloro(triethylenetetramine)-cobalt (III) chloride,[5] (**A**), and Ag_2O. These complexes were prepared as follows: 100 ml of a methanol solution of 8-quinolinol (4.35 g, 30 mmol) was slowly added to 100 ml aqueous solution of $[CoCl(OH)(trien)]^+$,[6] which was prepared from **A** of 9.35 g (30 mmol) and Ag_2O of 6.96 g (30 mmol). They were stirred for 30 hr at 50°, then complex **A** isomerizes to the coresponding β-form.[6] Precipitated yellowish-green tris(8-quinolinolato)cobalt(III) complex was filtered. The filtrate was concentrated on a rotary evaporator. The isolation of isomers was tried by using column chromatography of alumina. On elution with MeOH, the band of the complex split into three. The solution of first band was concentrated and dried over silicagel. Complex **1** was extracted with dry ethanol from the dried mixture and was recrystallized from ethanol–acetone (1: 2) three times. Complex **2** was extracted with dry methanol from the dried mixture and was recrystallized from water–acetone (1: 5) three times. Complex **1**: russet-colored crystals, yield: 2.14 g (15.6%), dec 237—238°. Complex **2**: yellowish-brown crystals, yield: 2.35 g (16.7%), dec 241—243°. *Anal.* Calcd for $CoC_{15}H_{28}Cl_2N_5O_3$ (MW 456.26): C, 39.49; H, 6.19; N, 15.35; Cl, 15.54. Found **1**: C, 39.78; H, 6.48; N, 15.20; Cl, 15.50. **2**: C, 39.47; H, 6.29; N, 15.13; Cl, 15.30. Complexes **1** and **2** are soluble in water, MeOH, DMSO,



α β_1 β_2

Fig. 1. The α, β_1 and β_2 Configurations of $[Co(oxine)(trien)]Cl_2\cdot 2H_2O$

---

[1] A. Ablov, *Bull. Soc. Chim. Fr.*, **53**, 234 (1933).

[2] *a*) T. Tanaka, M. Komura, Y. Kawasaki, and R. Okawara, *J. Organometal. Chem.*, **1**, 484 (1964); *b*) K. Kawakami and R. Okawara, *J. Organometal. Chem.*, **6**, 249 (1966).

[3] M.J. Frazer and Z. Goffer, *J. Chem. Soc.*, 1966, 544.

[4] S.K. Freeman and P.E. Spoerri, *J. Org. Chem.*, **16**, 438 (1951).

[5] A.M. Sargeson and G.H. Searle, *Inorg. Chem.*, **6**, 787 (1967).

[6] E. Kyuno, L.J. Boucher, and J.C. Bailar, Jr., *J. Am. Chem. Soc.*, **87**, 4458 (1965).

but are not soluble in most organic solvents. Complex **1** is much soluble in EtOH but **2** is somewhat soluble in EtOH. The third band of pink included the unreacted complex.

The IR spectrum of **1** has peaks at 3160, 3070, 2950, 2900, 1090 (s), 1064 (vs), 1037, 1003, and that of 2 has peaks at 3160, 3070, 2950, 2880, 1057 (vs), 1035 and 1008 cm^{-1}. This indicates that the complexes assumes the β-form.[7]

In the ^1H-NMR spectra of **1** and **2** in 3.6 mol D_2SO_4, the protons of both the NH and NH_2 groups of the coordinated trien of **1** showed four signals in the intensity ratio of 1: 3: 1: 1, while those of **2** showed five signals in the intensity ratio of 1: 1: 2: 1: 1. They disappeared in heavy water containing NaOH. It was reported by Buckingham that the order of chemical shift in ppm is $NHR_1R_2 < NH_2R < NH_3$.[8] Thus, in β_1 and β_2 also, the proton of the secondary NH of the coordinated trien is considered to absorb at lower fields than the terminal NH_2 protons. Also in the $[Co(sal)(NH_3)_4]^+$ ion,[9] it has been found that the NH_3 protons in a position trans to the coordinated carboxyl oxygen of the salicylato ligand absorb at the highest field, which is more electronegative than the phenoxy oxygen of that ligand. Again in the spectra of *cis*-β_2-[Co(sal)trien]$^+$ (**B**)[10] or *cis*-β_2-[Co(sar)trien]$^{2+}$ ions,[8a] the NH_2 protons in a position trans to the coordinated carboxyl oxygen of the salicyclato or sarcosinato ligand absorb at a higher field than those in a position *cis* to the coordinated carboxyl oxygen. As regards **1** and **2**, the signal of NH_2 group of **2** is at a higher field than that of **1**. Therefore the NH_2 group of **2** is considered at a position trans to the coordinated quinolinoxy oxygen of the 8-quinolinolato ligand, which is more electronegative than the nitrogen of the 8-quinolinol. Thus, **1** and **2** can be assigned to β_1 and β_2 respectively. While, the signal of the methylenecarbon protons of the coordinated trien of **1** showed one signal and that of **2** showed two signals. These results are similar to those of **B**.[10] Thus, **1** and **2** can be also assigned to β_1 and β_2 respectively. The observed chemical shifts (δ) of **1** are 2.45—3.77 (CH_2, 12H), 4.40 (NH_2, 1H), 4.55—5.37 (NH_2, 3H), 5.76, 5.93 (NH, each 1H) and 7.2—9.0 ppm (8-quinolinolato, 6H). Those of 2 are 2.43—3.24 (CH_2, 8H), 3.24—4.0 (CH_2, 4H), 4.30 (NH_2, 1H), 4.55 (NH_2, 1H), 5.03 (NH_2, 2H), 6.28 (NH, 1H) and 7.1—8.8 ppm (8-quinolinolato, 6H). Another signal of NH proton is overlapped with the signal of solvent.

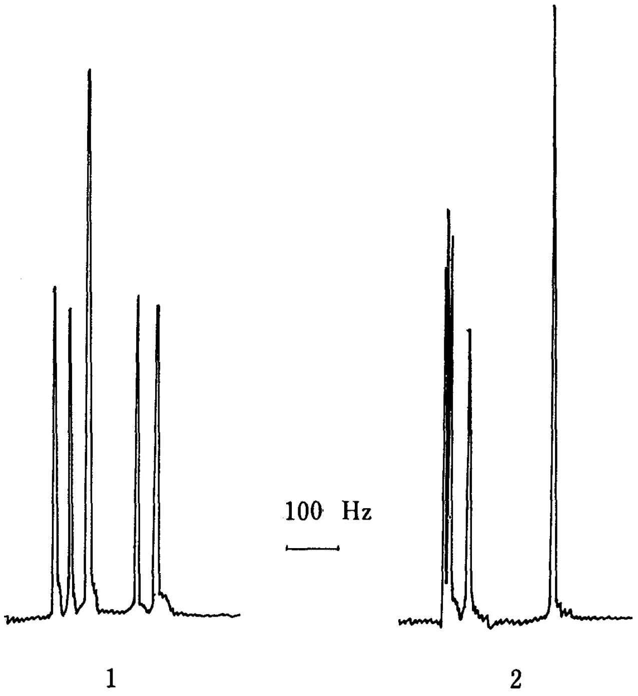


Fig. 2. The ^{13}C-NMR Spectra of Complexes 1 and 2 in D_2O

Standard: internal dioxane (δ=67.4 ppm).

---

[7] *a*) 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); *b*) D.A. Buckingham and D. Jones, *Inorg. Chem.*, **4**, 1387 (1965).

[8] *a*) L.G. Marzilli and D.A. Buckingham, *Inorg. Chem.*, **6**, 1042 (1967); *b*) D.A. Buckingham, L.J. Durham, and A.M. Sargeson, *Aust. J. Chem.*, **20**, 257 (1967).

[9] Y. Yamamoto, *Bull. Chem. Soc. Jpn.*, **51**, 2894 (1978).

[10] *a*) Y. Yamamoto and E. Toyota, *Bull. Chem. Soc. Jpn.*, **52**, 2540 (1979); *b*) Y. Yamamoto, E. Toyota, and N. Mitsudera, *ibid.*, in press.

In the ^{13}C-NMR spectra of **1** and **2** in heavy water, there have been observed nine signals for coordinated 8-quinolinolato ligand in the regions at 115—170 ppm. The methylene carbons of the coordinated trien have been observed five signals to each other. The signals of at 52.1 of **1** and at 43.3 ppm of **2** are overlapped. Although they are difficult to assign to the individual carbon atoms, they show two different configurations of β_1 and β_2 as is shown in Fig. 2. 43.4, 46.1, 52.1, 52.1, 54.5 and 56.5 for **1** and 43.3, 43.3, 54.1, 56.7, 56.8 and 57.2 ppm for **2**.

The equivalent conductance of **1** and **2** were Λ=250 and 241 S cm^2 in water respectively, while the absorption spectra of **1** and **2** in methanol have three absorption peaks at 325, 339 and 409 nm to each other. The peaks at 409 nm are based on the 8-quinolinolato-cobalt.[11] They are diamagnetic, and should be cobalt (III)complex of the low spin type.

Faculty of Pharmaceutical
Sciences, Higashi-Nippon-
gakuen University,
Ishikari-Tobetsu, Hokkaido,
061-02, Japan

YOSHIHISA YAMAMOTO
EIKO TOYOTA

Received August 2, 1980

---

11) K. Sone, *J. Am. Chem. Soc.*, **75**, 5207 (1953).