BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 2863—2864 (1971)

Preparation and Properties of Metal Complexes in Non-aqueous Solutions. III. Preparation of Tetrammine-monoethylenediamine- and -monopropylenediamine-cobalt(III) Complexes in Dimethyl Sulfoxide

Hayami YONEDA, Masayuki MUTO, and Kyoko TAMAKI
Department of Chemistry, Wakayama University, Masagocho, Wakayama

(Received March 24, 1971)

Tetramminemonoethylenediaminecobalt(III) complex is prepared by an indirect route[1]:

$$NH_4[Co(SO_3)_2(NH_3)_4] \xrightarrow{en} NH_4[Co(SO_3)_2(NH_3)_2en]$$
$$\xrightarrow{HCl} [CoCl_2(NH_3)_2en]Cl \xrightarrow{KNCS} [Co(NCS)_2(NH_3)_2en]^+$$
$$\xrightarrow{H_2O_2} [Co(NH_3)_4en]^{3+}$$

Such a roundabout method of preparation is necessary because of the lability of cobalt(III)ammine complexes in an alkaline solution. Even the basicity of ethylenediamine is enough to expel the coordinated ammonia from the coordination sphere. Previously Yoneda[2] suggetsed that cobalt(III)ammines are decomposed *via* the proton dissociation of the coordinated ammonia. That is, ammonia is linked to the cobalt(III) ion fairly firmly as long as it keeps its three hydrogen atoms and remains as NH_3, but it becomes labile when it loses a proton to form NH_2. If this interpretation is valid, we can expect that the monoethylenediamine complex can be prepared directly from the diacidotetrammine complex by using some non-aqueous solvent which prevents the proton dissociation of the coordinated ammonia. Thus, we tried to use dimethyl sulfoxide (DMSO) in the preparation of $[Co(NH_3)_4en]^{3+}$ and $[Co(NH_3)_4pn]^{3+}$ and obtained the expected results. The present paper will describe the details of the preparation and the PMR spectra of these two complexes.

Experimental

Preparation of the Complexes. Five grams (1/63 mol) of $[Co(NO_3)_2(NH_3)_4]NO_3$ were dissolved in 30 m*l* of DMSO, and to this solution there was added 0.95 g (slightly less than 1/63 mol) of ethylenediamine in 10 m*l* of DMSO. The solution was then kept at 60°C for three hours. Then, 130 m*l* of ethanol was added to precipitate the desired complex. Yield, 3.3 g. Orange crystals were obtained by recrystallization from a hot aqueous solution acidified with acetic acid. Found: C, 6.33; H, 5.47; N, 33.47%. Calcd for $[Co(NH_3)_4en](NO_3)_3$: C, 6.44; H, 5.41; N, 33.78%.

The monopropylenediamine complex was prepared in a similar way. Found: C, 9.09; H, 5.65; N, 32.68%. Calcd for $[Co(NH_3)_4pn]\ (NO_3)_3$: C. 9.30; H, 5.74; N, 32.56%.

PMR Measurements. The spectra reported here were recorded on a Varian A60 Analytical NMR spectrometer. The spectra were run in trifluoroacetic acid (TFA), and the chemical shifts were measured relative to tetramethylsilane as an internal reference.

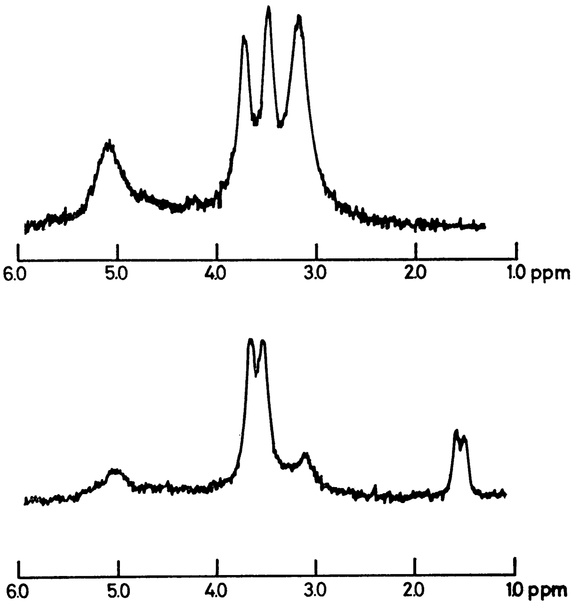

Fig. 1. The PMR spectra of $[Co(NH_3)_4en](NO_3)_3$ (above) and $[Co(NH_3)_4pn](NO_3)_3$ (below) in TFA.

---

[1] K. Ohkawa, J. Fujita, and Y. Shimura, This Bulletin, **38**, 66 (1965).

[2] H. Yoneda, *ibid.*, **31**, 74 (1958).

Table 1. Assignments of PMR signals of $[Co(NH_3)_4en](NO_3)_3$ and $[Co(NH_3)_4pn](NO_3)_3$ in TFA measured at 60MHz (ppm unit)

	CH_2CH_2	NH_3		NH_3			
$[Co(NH_3)_4en]^{3+}$	3.18	3.50	3.57	5.10			
	CH_3		CH_2	CH	NH_3		NH_2
$[Co(NH_3)_4pn]^{3+}$	1.50	1.58	3.08	*ca.* 3.33	3.53	3.67	5.0

Interpretation of the PMR Spectra

The PMR spectra of $[Co(NH_3)_4en](NO_3)_3$ and $[Co(NH_3)_4pn](NO_3)_3$ are shown in Fig. 1. The intensity ratios of the PMR signals in these spectra snd the comparison of these spectra with those of $[Co\ en_3]^{3+}$ and $[Co\ pn_3]^{3+}$ complexes lead to unambiguous assignments of these signals, as is shown in Table 1. Both spectra have the NH_3 signal in two separate peaks of equal intensity, which confirms that the complexes prepared are in fact $[Co(NH_3)_4en]^{3+}$ and $[Co(NH_3)_4pn]^{3+}$.