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The Preparation of Mixed Cobalt(III) Complexes of *N*,*N*-Bis(2-aminoethyl)glycine with the Carbonate or Oxalate Ion[1)]

Syoji NAKASHIMA and Muraji SHIBATA
Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa 920

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Synopsis. *mer*(N)- and *fac*(N)-[CoCO$_3$(*i*-dtma)] complexes have been prepared by the reaction of the tetradentate ligand with the [Co(CO$_3$)$_3$]$^{3-}$ complex. The corresponding [Coox(*i*-dtma)] complexes have been derived from the *mer*(N)-carbonato complex.

As to the cobalt(III) complex containing the tetradentate ligand *N*,*N*-bis(2-aminoethyl)glycine (abbreviated as *i*-DTMA) and the bidentate carbonate ion, two geometric isomers, *mer*(N) and *fac*(N), can possibly exist (Fig. 1). Of these, the *fac*(N) isomer has already been prepared by Schneider and Collman by means of a reaction between the [CoCl$_2$(*i*-dtma)] complex and lithium carbonate.[2)] We have now succeeded in obtaining the second isomer, *mer*(N), by means of a reaction of the *i*-DTMA on the tricarbonatocobaltate(III) complex.

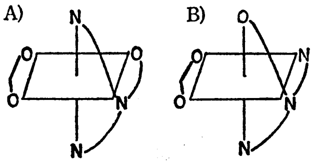

Fig. 1. Geometrical isomers of [CoCO$_3$(*i*-dtma)]
A: *mer*(N), B: *fac*(N).

The *i*-DTMA ligand was prepared from diethylenetriamine as a stock solution according to "Method B" described in the literature.[2)] A proper quantity (0.1 mol) of the *i*-DTMA stock solution was added to a fresly prepared solution of potassium tricarbonatocobaltate (III) (0.1 mol),[3)] and the mixture was stirred at room temperature for an hour. The resulting solution was charged on a column of a cation-exchange resin (Dowex 50WX8, Na-form). With careful washing with water, two bands, colored pink-violet and red-violet, descended the column, and the effluent was collected in two fractions. For convenience, these fractions were labeled "E-1" and "E-2". Each fraction was concentrated, and a small amount of a mixture of ethanol and ether was added to the concentrate; then the mixture was kept in a refrigerator. Very fine crystals were obtained from each concentrate. The complexes obtained from E-1 and E-2 were tentatively identified as *mer*(N) and *fac*(N) respectively, based on the order of elution.[4,5)] The yields were about 6 g for *mer*(N) and about 9 g for *fac*(N). Found for *mer*(N): C, 29.40; H, 5.40; N, 14.56%. Calcd for [CoCO$_3$(C$_6$H$_{14}$N$_3$O$_2$)]·0.5H$_2$O: C, 29.18; H, 5.25; N, 14.58%. Found for *fac*(N): C, 30.05; H, 5.29; N, 15.07%. Calcd for [CoCO$_3$(C$_6$H$_{14}$N$_3$O$_2$)]: C, 30.12; H, 5.06; N, 15.05%.

Two related complexes, *mer*(N), and *fac*(N)-[Coox(*i*-dtma)], were derived from the *mer*(N)-[CoCO$_3$(*i*-dtma)] complex. After the hydrolysis of the carbonato complex (10 g) by 60% HClO$_4$, a proper amount of potassium oxalate was added to the acid solution; then it was neutrallized with an aqueous solution of potassium hydroxide. After the removal of the precipitated material, the resulting solution was chromatographed in the same manner as the carbonato complexes. The two bands corresponding to the *mer*(N)- and *fac*(N)-isomers descended. The crystals of these isomers were obtained in the same manner as before. The yields were 3 g for *mer*(N) and 2 g for *fac*(N). Found for *mer*(N): C, 30.50; H, 4.71; N, 13.20%. Calcd for [Coox(C$_6$H$_{14}$N$_3$O$_2$)]·0.5H$_2$O: C, 30.39; H, 4.78; N, 13.29%. Found for *fac*(N): C, 31.12; H, 4.72; N, 13.73%. Calcd for [Coox(C$_6$H$_{14}$N$_3$O$_2$)]: C, 31.28; H, 4.59; N, 13.68%.

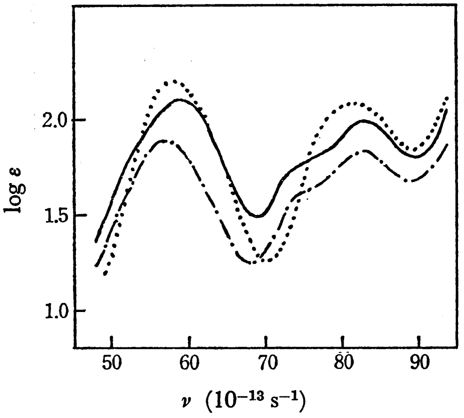

Fig. 2. Absorption spectra of *mer*(N)-[CoCO$_3$(*i*-dtma)] (——), *fac*(N)-[CoCO$_3$(*i*-dtma)] (⋯⋯) and *mer*(*trans*)-[CoCO$_3$(gly)(NH$_3$)$_2$] (—·—).

The absorption spectra of the two carbonato complexes are shown in Fig. 2. The spectrum of the complex obtained from E-2 shows the first absorption band ($\nu_{\rm I}$) at $58.0\times10^{13}\,{\rm s}^{-1}$ (log ε=2.21) and the second band ($\nu_{\rm II}$) at $81.5\times10^{13}\,{\rm s}^{-1}$ (log ε=2.11). These values agree fairly with those for the known *fac*(N) complex ($\nu_{\rm I}$=58.5, $\nu_{\rm II}$=81.5).[2)] From this it can be judged that this complex is the *fac*(N)-isomer. On the other hand, the spectrum of the complex obtained from E-1 shows the $\nu_{\rm I}$ at $58.1\times10^{13}\,{\rm s}^{-1}$ (log ε=2.12) and the $\nu_{\rm II}$ at $82.3\times10^{13}\,{\rm s}^{-1}$ (log ε=1.98). In addition, this spectrum exhibits a shoulder at *ca.* $74.5\times10^{13}\,{\rm s}^{-1}$ (log ε=1.7). A similar spectrum shape has been reported with the *mer*(*trans*)-[Co(CO$_3$)(gly(NH$_3$)$_2$] complex (*trans* refers to the two NH$_3$ groups).[6)] The spectrum is included in Fig. 2. Although some hypsochromic shifts in the ν_{I} and ν_{II} bands can be seen in the present complex, the position of the shoulder scarcely shifts at all. From this similarity in spectrum, the present complex can be assigned to the *mer*(N)-isomer.

The PMR spectra of the same complexes are shown in Fig. 3. The E-1 or *mer*(N) complex shows a singlet at 3.75 ppm which has its origin in the methylene protons of the acetate group in the chelated *i*-DTMA, while the E-2 or *fac*(N) complex shows a quartet with the AB pattern at 3.80—4.25 ppm. These results confirm the assignments based on the absorption spectra.

As to the corresponding oxalato complex, the isomer obtained from the second fraction in chromatographic separation showed an absorption spectrum similar to that of the *fac*(N)-isomer of the carbonato complex except for hypsochromic shifts due to a higher ligand field: $\nu_{\mathrm{I}}=57.9\times10^{13}\,\mathrm{s}^{-1}$ (log $\varepsilon=2.19$), $\nu_{\mathrm{II}}=82.6\times10^{13}\,\mathrm{s}^{-1}$ (log $\varepsilon=2.25$). This fact indicates that this isomer has the *fac*(N) geometry. As to the isomer obtained from the first fraction, the gross features of the spectrum correspond well to those of the *mer*(N)-isomer of the carbonato complex except for the disappearance of a shoulder at *ca.* $74.5\times10^{13}\,\mathrm{s}^{-1}$. Thus, this complex can be identified as the *mer*(N)-isomer.

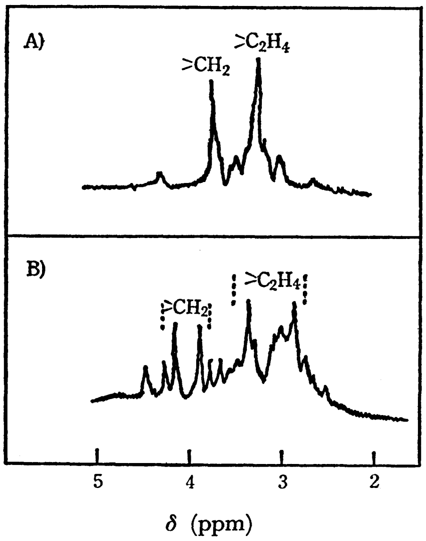

Fig. 3. PMR spectra of [CoCO$_3$(*i*-dtma)] (in D$_2$O, δ *vs.* DSS).
A: *mer*(N), B: *fac*(N).

In a previous paper,[7] it has been said that a cobalt (III) complex consisting of a five-membered α-aminoacidate ring, two NH_3 groups in the *trans* position, and a four-membered carbonate ring reveals a shoulder which may be considered to be one component of the split second absorption band. This remark can now be modified as follows: such a shoulder appears even though the two NH_3 groups and a NH_2 group of an α-aminoacidate ion are replaced by a diethylenetriamine backbone (NNN).

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