Isomerism of the Metal Complexes Containing Multidentate Ligands. VI. Geometric and Optical Isomers of the Tris(*meso*-2,3-butanediamine)-cobalt(III) Complex

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(Received February 19, 1975)

The tris(*meso*-2,3-butanediamine)cobalt(III) complex was prepared, and four possible isomers, *mer*-Λ, *mer*-Δ, *facial*-Λ, and *facial*-Δ, were isolated by column chromatography on SP-Sephadex in the formation ratio of 1.4 : 1.4 : 1.0 : 1.0. The configurations and conformations of these isomers were proposed on the basis of the electronic, the circular dichorism, and the PMR spectra.

When unsymmetric bidentate ligands such as *R*-1,2-propanediamine(*R*-pn)[2] and 2-methyl-1,2-propanediamine(ibn)[3] coordinate to the cobalt(III) ion, geometric(*mer* and *facial*) isomers are formed by the positions of the methyl groups in addition to the optical isomers(Δ and Λ); they have been isolated and characterized. When a symmetric ligand with a *meso* structure like *meso*-2,3-butanediamine(mbn) coordinates, geometric isomers(*mer* and *facial*) are formed by the alignment of two asymmetric carbons(*R* and *S*) for each of the absolute configurations, Δ and Λ (Fig. 1). Theoretically eight(lel_3, $3lel_2ob$, $3lelob_2$, ob_3) and four (lel_3, lel_2ob, $lelob_2$, ob_3) energetically unique conformational isomers are expected for the *mer* and *facial* isomers respectively, but a rapid inversion of the chelate rings in solution will make only four isomers detectable: *mer*-Λ, *mer*-Δ, *facial*-Λ, and *facial*-Δ (Fig. 1).

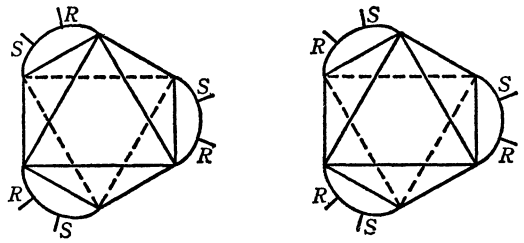

Fig. 1. Geometric isomers of Λ-$[Co(mbn)_3]^{3+}$.

The tris(*meso*-2,3-butanediamine)cobalt(III) complex was first studied by Woldbye,[4] but no geometric isomer was separated and only optical isomers with low optical activities were obtained. In the present paper the isolation of four possible isomers in a pure state and their characterization will be presented.

Experimental

Ligands. A mixture of *meso* and *racemic* 2,3-butanediamine was prepared by the reduction of dimethylglyoxime with Raney nickel in alkaline solution;[5] the isomers were then separated by the procedure of Dickey *et al.*[5]

Preparation of the Complex. *Meso*-2,3-butanediamine hydrochloride(1.3 g, 8.1 mmol) was dissolved in 5 ml of water, and the solution was adjusted to pH 8 by adding a concd. NaOH solution. To this solution, $[CoBr(NH_3)_5]Br_2$ (0.9 g, 2.3 mmol) and active charcoal (0.3 g) were added, after which the mixture was stirred for from one to three days at room temperature. The brown solution thus obtained was directly subjected to column chromatography on SP-Sephadex after the removal of charcoal.

Chromatographic Separation of the Isomers. On the top of the adsorbent layer of an SP-Sephadex column (ϕ 2.7 × 120 cm), the same SP-Sephadex, saturated in advance with a prepared solution containing about 0.4 mmol of the complex, was poured; the complex was subsequently eluted by a 0.18 M sodium $(+)_{589}$ tartratoantimonate(III) solution* at a rate of 0.75 ml per minute. The effluent was separated into fractions of 15 ml each, and the absorbance at 470 nm was plotted against the eluate volume (Fig. 2). Two separated peaks, A and B, were thus obtained, but as each peak seemed to be a mixture of enantiomers, the fractions were again adsorbed on SP-Sephadex after dilution with water, and subsequently eluted with a 0.20 M sodium $(+)_{589}$ tartrate solution. Figure 3 shows the elution curve of the fractions corresponding to the band A. Two separated peaks, A-1

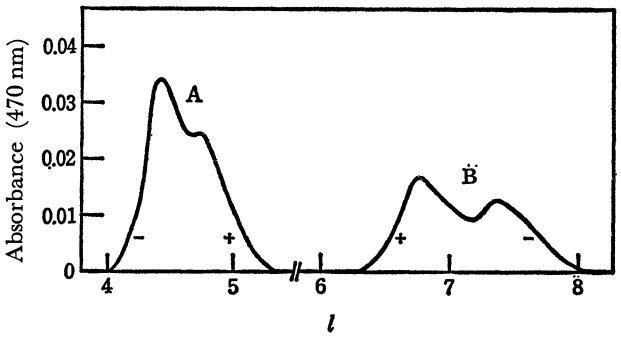

Fig. 2. Elution curve of the isomers of $[Co(mbn)_3]^{3+}$. Eluent: 0.18 M sodium $(+)_{589}$ tartratoantimonate-(III).

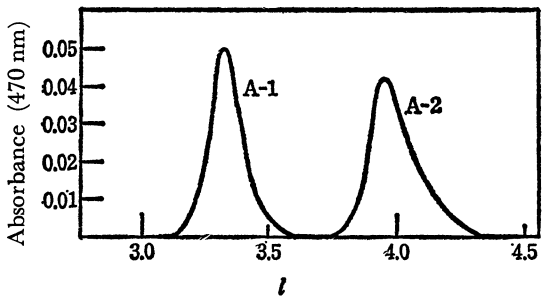

Fig. 3. Elution curve of the fractions corresponding to the band A of Fig. 2.
Eluent: 0.20 M sodium $(+)_{589}$ tartrate.

* The concentration was calculated on the basis of the formula: $[Sb_2(C_4H_2O_6)_2]^{2-}$.

and A-2, appeared. Two peaks similarly separated from the peak B were named B-1 and B-2, in the order of elution. Thus, four isomers, A-1, A-2, B-1, and B-2, were isolated. Found: A-1, C, 29.34; H, 8.56; N, 17.20%. A-2, C, 29.45; H, 8.66; N, 17.26%. B-1, C, 29.15; H, 8.63; N, 17.19%. B-2, C, 29.10; H, 8.96; N, 17.04%. Calcd for $[Co(mbn)_3]Cl_3 \cdot 3.5\ H_2O$ ($C_{12}H_{43}O_{3.5}N_6CoCl_3$): C, 29.25; H, 8.80; N, 17.05%.

Measurements. The electronic absorption(AB) and circular dichroism(CD) spectra were measured at 25 °C, as has been reported previously.[1] The 100 MHz PMR spectra were measured in D_2O by means of a JEOL JNM-MH-100 spectrometer. A small amount of a concd. NaOD-D_2O solution was added to deuterate the amine protons. DSS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate) was used as the internal reference.

Results and Discussion

(1) *PMR Spectra.* Figures 4a and 4b show the PMR spectra of *N*-deuterated A-1 and B-1 isomers respectively. Although the ligand $ND_2CH(CH_3)CH(CH_3)ND_2$ in the *gauche* conformation can give rise to the eight-spin system of the $X_3AA'X'_3$ type, the spin-spin coupling constants $J_{XX'}$ and $J_{AX'}=J_{A'X}$ are considered to be approximately zero. For both isomers, the peaks at 1.1—1.4 ppm and 2.9—3.6 ppm were assigned to the methyl and methine protons respectively.

As the *facial* isomer has three equivalent chelate rings(Fig. 1), two doublet signals due to the axial and equatorial methyl protons are expected unless the chelate rings assume a symmetric envelope conformation. On the other hand, the *mer* isomer, which has no symmetry axis of rotation and which belongs to the point group C_1, should show more complicated methyl signals consisting of up to six doublets. Actually, the A-1 and B-1 isomers showed three and two methyl doublets respectively; the *mer* and *facial* forms were assigned to them.

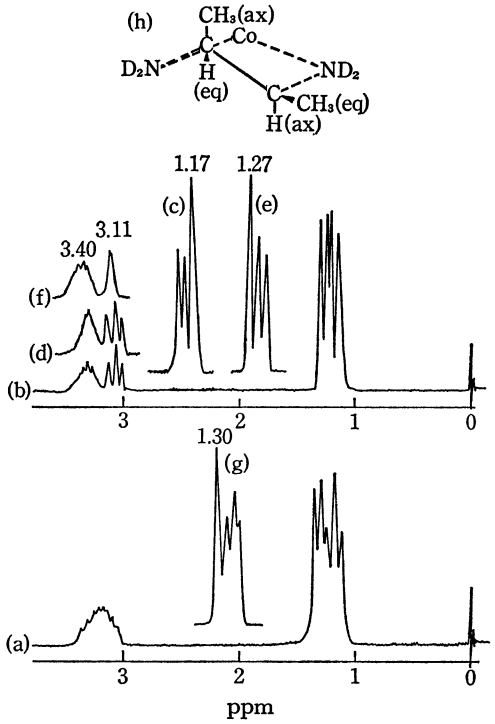

Fig. 4. 100 MHz PMR spectra of the isomers A-1 (a) and B-1 (b).
Double resonance spectra irradiated at $\delta=3.40$ ppm (c), 1.17 ppm (d), 3.11 ppm (e), and 1.27 ppm (f) of the isomer B-1. The methyl part of double resonance spectrum irradiated on the methine signal (3.15 ppm) of the isomer A-1 (g). δ-Conformation of the mbn chelate ring (h).

The methine proton signals of the *facial* isomer consist of two components, and the resonances centered at 3.11 ppm are considered as axial methine proton signals, by analogy with the methylene proton signals of $[Co(CN)_4(R\text{-pn})]^-$ [6] and $[Co(pn)_3]^{3+}$.[7] The nuclear magnetic double-resonance technique was used to clarify the spin-spin coupling between methyl and methine protons(Figs. 4c—4g). For the *facial* isomer, irradiation at the methine signals (3.40 ppm) converted the methyl doublet(1.17 ppm, $J_{H\text{-}CH_3}=7$ Hz) into a sharp singlet(Fig. 4c), indicating that it originates from the axial methyl protons. Conversely, the irradiation of the doublet at 1.17 ppm made the methine signals (3.40 ppm) decouple to a still broad peak (Fig. 4d). This broadening is probably due to the spin-spin coupling between two methine protons and the strong scalar coupling with the Co-59 quadrupolar nucleus ($I=7/2$)[8] in the *gauche* conformation. Similarly, the methine signals centered at 3.11 ppm couple with the methyl protons (1.27 ppm, $J_{H\text{-}CH_3}=7$ Hz) (Figs. 4e and 4f); this doublet corresponds to the equatorial methyl group. These methyl protons have an additional bond removed from the central cobalt atom compared with the methine protons and are apparently not affected by the coupling with the Co-59 nucleus.[8]

As for the *mer* isomer, its spectrum is too complicated to be analyzed accurately. Irradiation at the methine signals (3.15 ppm) converted the lower methyl doublet (1.30 ppm) into a singlet (Fig. 4g).

It is to be noted that the $[Co(mbn)_3]^{3+}$ and $[Co(ibn)_3]^{3+}$ ions show chemichal-shift differences between the axial and equatorial methyl groups, whereas the $[Co(NH_3)_4(mbn)]^{3+}$ and $[Pt(mbn)_2]^{2+}$ ions[9] show none, giving only one sharp methyl doublet; in the latter complexes, the two methyl groups are indistinguishable upon rapid chelate ring inversion at room temperatures. However, the proton-decoupled ^{13}C-NMR spectrum of $[Co(en)_2(mbn)]^{3+}$ and $[Co(en)_2(ibn)]^{3+}$ shows two methyl signals[10] due to the axial and equatorial methyl groups. These facts indicate that the axial and equatorial methyl groups in tris(diamine)metal complexes are magnetically nonequivalent because of the unequal energy of the *lel* and *ob* conformations, even when chelate ring inversion is rapid. This chemical-shift difference[11] between axial and equatorial methyl protons was used for the conformational analysis. The difference in the B-1 (*facial*) isomer is 0.10 ppm (=1.27—1.17 ppm), slightly larger than that (0.07 ppm) of the *facial*-$[Co(ibn)_3]^{3+}$.[3] For *meso*-2,3-butanediamine-*N*,*N*,*N'*,*N'*-tetraacetatocobaltate(III), in which the diamine part is considered to be fixed in the *gauche*

Table 1. Absorption and circular dichroism spectra (in cm^{-1})

Isomer	First band		Second band		CT band	
	AB	CD	AB	CD	AB	CD
A-1 (*mer*-Λ)	21100(102)	20300(+2.92) 23400(−0.08)	29400(94)	28100(+0.32)	46900(24600)	45500(−34) 51800(+11)
A-2 (*mer*-Δ)	21100(102)	20300(−2.91) 23500(+0.08)	29400(94)	28100(−0.32)	46700(23600)	45500(+32) 52100(−10)
B-1 (*facial*-Λ)	21100(109)	20300(+3.28) 23400(−0.12)	29400(98)	28100(+0.36)	46900(24100)	45500(−32) 52400(+14)
B-2 (*facial*-Δ)	21100(106)	20300(−3.13) 23400(+0.12)	29400(96)	28100(−0.36)	46900(24700)	45700(+33) 52400(−13)

Molar extinction coefficients(ε) and $\Delta\varepsilon$ values are given in parentheses.

conformation, the chemical-shift difference has been reported to be 0.16 ppm.[12] These facts indicate that the B-1(*facial*) isomer in this case has chelate rings with non-symmetric gauche conformations.

It has been concluded for the Λ-$[Co(S\text{-pn})_3]^{3+}$ ion[8] that the ligands exist primarily in one conformation with the equatorial methyl group, and that the observed difference, 0.35 ppm, can be taken as the difference between the axial and equatorial methylene protons. If this result can be used to interpret the spectrum of the *facial*-Λ-$[Co(mbn)_3]^{3+}$ ion, the difference between the axial and equatorial methine protons, 0.29 ppm (=3.40—3.11), may suggest that the ligand mbn is primarily in the $\delta\delta\delta(lel_3)$ conformation (*cf.* (2)).

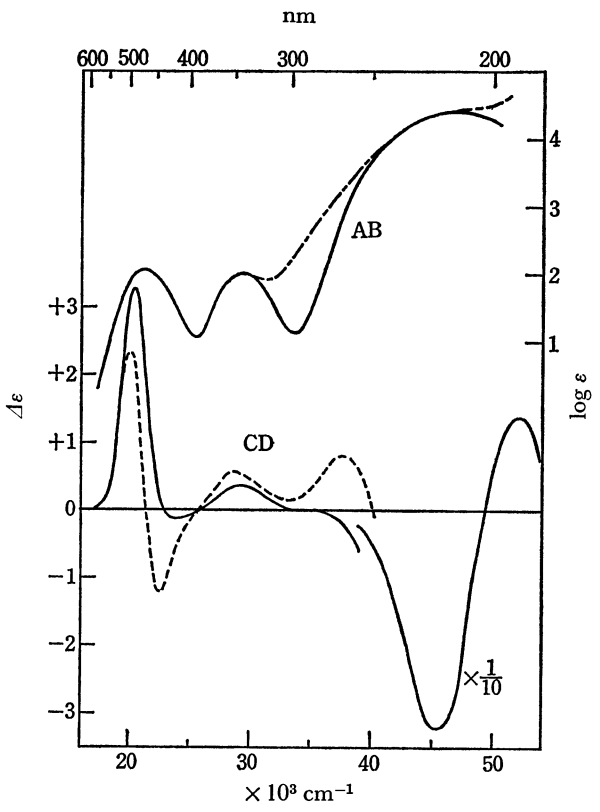

Fig. 5. AB and CD spectra of the isomer B-1(*facial*-Λ); —— in water, ---- and ---- in 0.2 M Na_3PO_4 solution.

For the A-1(*mer*) isomer, the ligand seems to assume a more distorted conformation than for the B-1(*facial*) isomer, because: (a) the methine signals appear in a broad peak, (b) the *mer* isomer is energetically less stable than the *facial* isomer(*cf.* (3)), and (c) the A_2 component in the CD spectrum is weak(*cf.* (2)).

(2) *Absorption and Circular Dichroism Spectra.* The AB and CD spectral data are listed in Table 1. The rotations shown by the fractions corresponding to the four peaks, A-1, A-2, B-1, and B-2, are +, −, +, and − for 589 nm. The first absorption maxima of $[Co(mbn)_3]^{3+}$ (473 nm) and $[Co(ibn)_3]^{3+}$ [3] (480 nm) are in a lower energy region than that of the Λ-$[Co(R\text{-pn})_3]^{3+}$ ion (467 nm). The shift may be due to two methyl groups of the ligand, mbn or ibn, one of them being forced to be in the axial position regardless of the chelate ring (δ or λ).

The CD spectrum of the B-1 isomer resembles that of Λ-$[Co(en)_3]^{3+}$ in both the d-d and charge-transfer regions (Fig. 5). Thus, taking the PMR results into account, its absolute configuration can tentatively be determined to be *facial*-Λ. Similarly, the configurations of the isomers A-1, A-2, and B-2 are determined to be *mer*-Λ, *mer*-Δ, and *facial*-Δ respectively. The AB and CD spectra of two geometric isomers, *mer* and *facial*, are similar in shape, but the peak intensities of the former are slightly lower than those of the latter (Table 1).**

The negative CD component at 427 nm corresponding to the higher-energy band in the first absorption region is slightly weaker for the *mer* than the *facial* isomer (A-1). This peak is enhanced to the same intensity for both isomers in a 0.2 M sodium phosphate solution, and it is assigned to the $A_2(D_3)$ component. There is a general tendency for the A_2 com-

** A sample of $(+)_{589}[Co(mbn)_3]Br_3$ resolved by the fractional crystallization of the diastereoisomer with $(+)_{589}$ nitrocamphor[4] was kindly provided by Prof. F. Woldbye, which showed a small CD intensity with the constant value of $\Delta\varepsilon(20240\ cm^{-1})/\varepsilon(21200\ cm^{-1}) = 22.7\times10^{-4}$. Chromatographic separation revealed this to be a mixture of four isomers, *mer*-Δ, *mer*-Λ, *facial*-Λ, and *facial*-Δ, in the ratio 1.8 : 2.2 : 1.2 : 1.0; the composition explained the low optical activity previously reported,[4] *i.e.* the incomplete resolution.

ponent of the tris(diamine)cobalt(III) complexes to become weak as the chelate ring deviates from the *lel* conformation. The *mer* isomer has, therefore, a more distorted conformation than the *facial* isomer. In the above sodium phosphate solution, a new, weak CD peak appeared at 264 nm ($\Delta\varepsilon = +0.80$ for the *facial*-Λ isomer) as a result of the ion-pair formation, this peak is characteristic of the *lel* conformation.[13]

(3) *Formation Ratio.* If the relative abundance of geometric isomers is governed by statistics alone, the ratio of the *mer* isomer to the *facial* isomer should be 3 : 1; *i.e.*, 75% of the $[Co(mbn)_3]^{3+}$ formed should be the *mer* isomer. The actual formation ratio, as calculated from the area of the elution peaks and the extinction coefficients at 470 nm ,was A-1 : A-2 : B-1 : B-2 = 1.4 : 1.4 : 1.0 : 1.0; the formation of the B isomers (*facial*) was therefore more favored than the statistically calculated ratio. From the above data, the apparent free energies of the isomers at 300 K were calculated to be 0 for the *facial* isomer (B) and −0.2 kcal/mol for the *mer* isomer (A). An entropy contribution to the free energy from the 1 : 3 statistical weighting of the two configurations, *facial* and *mer*, must be taken into account. The calculated enthalpies and other entropy contributions give rise to relative energies of the following order: *facial* isomer = 0 and *mer* isomer = 0.5 kcal/mol. This value is in good agreement with the result, 0.7 kcal/mol, of the conformational analysis calculated by Niketic and Woldbye.[14]

(4) *Effects of the Eluents on the Separation Order of the Isomers.* As has been described above, when $(+)_{589}$ tartratoantimonate(III) was used as the first eluent, the isomers were eluted in the order: (A-2+A-1), (B-1+B-2) (Fig. 2), whereas with sodium $(+)_{589}$ tartrate as the eluent, four isomers were eluted in the order: (A-1+B-1), (A-2+B-2), and each peak, the mixture of the geometric isomers, was further separated by sodium $(+)_{589}$ tartratoantimonate(III). Thus, sodium $(+)_{589}$ tartratoantimonate(III) is effective in separating geometric isomers, whereas sodium $(+)_{589}$ tartrate in resolving optical isomers on an SP-Sephadex column. The geometric isomers of the $[Co(mbn)_3]^{3+}$ ion were completely separated by a 0.16 M sodium sulfate solution as well.

The X-ray determination of the absolute configuration of the *facial*-Λ-isomer is now under way in the laboratory of Professor Y. Saito, the University of Tokyo.

We are grateful to Professor F. Woldbye, the Technical University of Denmark, for providing the sample.

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