Isomerism of the Metal Complexes Containing Multidentate Ligands. III. Geometric and Optical Isomers of the Tris(2-methyl-1,2-propanediamine)cobalt(III) Ion[1]

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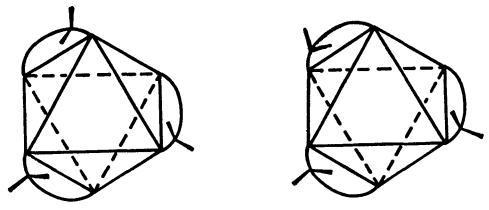
The tris(2-methyl-1,2-propanediamine)cobalt(III) complex was prepared, and four possible isomers, geometrical and optical, were isolated by column chromatography on SP-Sephadex. Their configurations were assigned on the basis of the formation ratio and electronic, infrared, circular dichroism and PMR spectra: they were later confirmed by X-ray analysis.

For a tris(diamine) complex with a symmetrical bidentate ligand like ethylenediamine, only a pair of optical isomers are formed, whereas for a complex with an unsymmetrical bidentate ligand geometrical isomers can be expected in addition to optical isomers. In 1968 MacDermott[2] separated *mer* and *facial* isomers of Δ-[Co(*l*-pn)$_3$]$^{3+}$* as the chloride and bromide by the gradual evaporation of their aqueous solutions, and found that the physical properties were similar for these two isomers. More recently, Crossing and Snow[3] tried to study the *mer* isomer by X-ray structure analysis, but they failed to find good crystals for their purpose.

With unsymmetrical 2-methyl-1,2-propanediamine (*iso*-butylenediamine, abbreviated as ibn) as the ligand, the isolation and characterization of four isomers, geometrical and optical, of the tris(ibn)cobalt(III) complex will be described in this paper (*cf.* Fig. 1).



Δ(*facial*) Δ(*mer*)

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

Experimental

Measurements. All the measurements were done in the same way as in the previous papers.[1]

Ligand. The *iso*-butylenediamine was obtained from the Aldrich Chem. Co., U.S.A., and was used without further purification.

Preparation of the Complex. To 3.8 g (10 mmol) of [CoBr(NH$_3$)$_5$]Br$_2$ suspended in 50 ml of water, 3 g (34 mmol) of the ligand was added. After 0.5 g of active charcoal had been added, the mixture was stirred for several days at room temperature; the brown solution thus obtained was directly subjected to column chromatography on SP-Sephadex after the removal of the charcoal.

Chromatographic Separation of the Isomers. A column chromatographic method on ion-exchange Sephadex developed by us[4] was used to separate and, at the same time, resolve the isomers. The SP-Sephadex C-25 used was a product of Pharmacia, Sweden, which has sulfopropyl groups as the cation-exchange group. An SP-Sephadex column of ϕ2.7 cm × 130 cm was prepared; on the top of the adsorbent layer, the same SP-Sephadex, saturated in advance with the prepared complex solution, was poured so as to make a layer about 5 mm thick. As the eluent we used a 0.15 M sodium (+)$_{589}$-tartrate solution with an elution velocity of 0.4—0.5 ml per minute. Under these conditions, 7—10 days were required for the complete elution of the complex, which produced three separate bands, I, II, and III (Fig. 2). The effluent was separated into fractions of 15 ml each, and the absorbance of each fraction at 475 nm (cell thickness, 1 cm) was plotted against the volume ratio of the effluent (V) *versus* the bed volume of the column (V_t=750 ml). The isomers corresponding to the fastest and

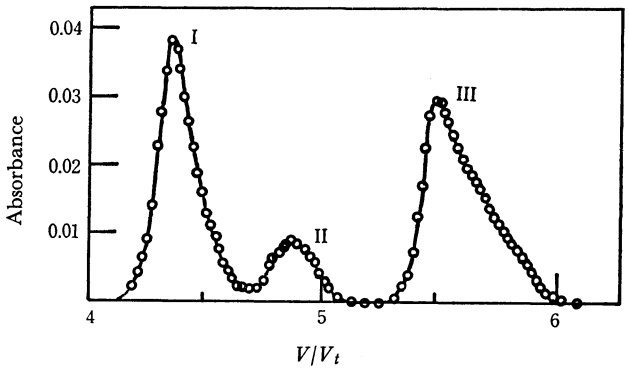


Fig. 2. Elution curve.
Eluent: 0.15 M sodium (+)$_{589}$-tartrate solution.

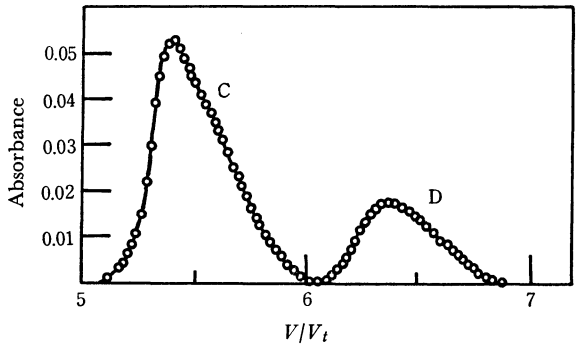


Fig. 3. Elution curve of the fractions corresponding to the peak III of Fig. 2.
Eluent: 0.3 M sodium (+)$_{589}$-tartratoantimonate(III).

* *l*-pn denotes (−)$_{589}$-propylenediamine.

1) A part of the present investigation was presented at the 14th ICCC, Toronto, Canada, June, 1972. Parts I and II were published in This Bulletin, **45**, 179, 3451 (1972).

2) T. E. MacDermott, *Inorg. Chim. Acta*, **2**, 81, (1968).

3) P. F. Crossing and M. R. Snow, *J. Chem. Soc., Dalton*, **1972**, 295.

4) Y. Yoshikawa and K. Yamasaki, *Inorg. Nucl. Chem. Lett.*, **6**, 523 (1970).

Table 1. Chemical compositions of the isomers

Complex	Elemental analyses (Calcd. value)			
	Co (%)	C (%)	H (%)	N (%)
A: $[Co(ibn)_3]Cl_3 \cdot 4H_2O$	11.84 (11.74)	28.71 (28.72)	8.53 (8.84)	16.87 (16.75)
B: $[Co(ibn)_3]Cl_3 \cdot 3H_2O$	12.11 (12.18)	30.08 (29.79)	7.84 (8.75)	17.15 (17.37)
C: $[Co(ibn)_3]Cl_3 \cdot 4H_2O$	11.85	29.06	8.35	17.03
D: $[Co(ibn)_3]Cl_3 \cdot 3H_2O$	11.84	29.76	8.02	17.04

middle peaks, I and II, were named A and B respectively. All these fractions were optically active, the signs of both I and II being plus, and that of the slowest III being minus for the Na–D line; their area ratio was 3 : 1 : 4. As the III peak had a small shoulder and seemed to be a mixture of isomers, the fractions corresponding to the III peak were diluted 4—5 times with water; then they were again adsorbed on SP-Sephadex, this time a 0.3 M sodium $(+)_{589}$-tartratoantimonate(III) being used as the eluent. The elution curve showed two peaks; these isomers were named C and D respectively (Fig. 3). Thus, the area ratio of the four peaks corresponding to the A, B, C, and D isomers was 3 : 1 : 3 : 1; no further separation was possible, not even by repeated chromatography.

Purification of the Isomers. The isomers separated as the tartrates and tartratoantimonates(III) were converted into chlorides by adsorption on SP-Sephadex, followed by elution by a 1 M sodium chloride solution. These chlorides were precipitated as hexacyanocobaltates; they were then again converted into chlorides by the anion-exchange resin, as has been described before.[1] The four isomers have the chemical compositions shown in Table 1.

Effects of Eluents on the Separation Order of the Isomers. As we have described above, these four isomers were eluted by sodium $(+)_{589}$-tartrate in the order of A, B, and (C+D); the subsequent separation of the last mixture into C and D was accomplished by sodium $(+)_{589}$-tartratoantimonate(III). If sodium $(+)_{589}$-tartratoantimonate(III) was used first, the order of separation was A, C, and (B+D), and the last mixture was further separated by sodium $(+)_{589}$-tartrate. Thus, sodium $(+)_{589}$-tartratoantimonate(III) is effective in separating geometric isomers, whereas sodium $(+)_{589}$-tartrate is effective in separating optical isomers. Sodium $(+)_{589}$-tartratoarsenate(III) was prepared and tested for separation with the same results as for sodium $(+)_{589}$-tartratoantimonate(III).

Results and Discussion

Absorption (AB) and Circular Dichroism (CD) Spectra. In Fig. 4 the AB and CD spectra of the B isomer are shown, while Tables 2 and 3 list their data. The maximum of the octahedral $^1T_{1g} \leftarrow {}^1A_{1g}$ absorption (480 nm) is at a longer wavelength than the $[Co(en)_3]^{3+}$ (467 nm) and Λ-$[Co(l\text{-pn})_3]^{3+}$ (467 nm) ions; the shift may be due to the two methyl groups of the ligand, since one of them is forced to be in the axial position regardless of the chelate-ring conformation(δ or λ). The CD band corresponding to the first absorption band is at 494 nm ($\Delta\varepsilon$=3.00), which splits into two at 503 nm ($\Delta\varepsilon$=2.16) and 450 nm ($\Delta\varepsilon$=−1.08) upon the addition of sodium phosphate, the presence of the

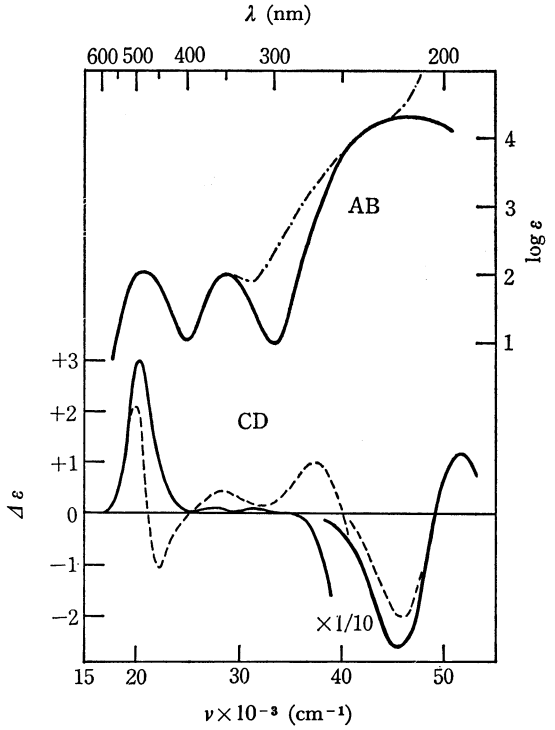


Fig. 4. AB and CD spectra of the isomer B; —— in water, —·— and ---- in 0.2 M Na_3PO_4 solution.

Table 2. Absorption spectra (in cm^{-1})

Complex	First Band $^1A_{1g} \rightarrow {}^1T_{1g}$	Second Band $^1A_{1g} \rightarrow {}^1T_{2g}$	CT Band $N(\sigma) \rightarrow e_g(\sigma^*)$
A(Λ-*mer*)	20800 (108)	28800 (101)	46300 (20400)
B(Λ-*facial*)	20800 (110)	28800 (102)	46500 (20400)
C(Δ-*mer*)	20800 (107)	28800 (100)	46500 (21400)
D(Δ-*facial*)	20800 (112)	28800 (106)	46500 (20400)

CT: Charge transfer
Molar extinction coefficients (ε) are given in parentheses.

Table 3. Circular dichroism spectra (in cm^{-1})

Complex	First band	Second band	CT band
A(Λ-*mer*)	20200 (+2.80)	27500 (+0.18) 30600 (+0.12)	45100 (−27) 51600 (+ 9)
B(Λ-*facial*)	20200 (+3.00)	27600 (+0.12) 30800 (+0.09)	45300 (−26) 51800 (+12)
C(Δ-*mer*)	20200 (−2.79)	27500 (−0.18) 30300 (−0.12)	45100 (+29) 51800 (−11)
D(Δ-*facial*)	20200 (−2.99)	27400 (−0.12) 30300 (−0.08)	45300 (+26) 52400 (−12)

$\Delta\varepsilon$ values are given in parentheses.

Table 4. Some characteristic IR bands of the isomers A and B (in cm^{-1})

A(*Λ-mer*)	1300(m)	1268(m)	1098(sh)	—	890(m)	814(m)
B(*Λ-facial*)	1313(m)	1258(m)	—	1050(w)	897(m)	829(m)

m: medium, w: weak, sh: shoulder

A_2 component being disclosed (Fig. 4). At the same time, a new CD band appears at 266 nm ($\Delta\varepsilon=0.98$) which corresponds to the charge-transfer absorption due to ion-pair formation. This CD band is characteristic of the *lel* conformation, and has never been observed for an *ob* conformation like *Δ*-$[Co(d\text{-pn})_3]^{3+}$ ion.[5] The CD spectrum of the A isomer is almost the same as that of B (Table 3). The C and D isomers show almost the identical CD spectra, with the sign opposite to that of the B isomer. The AB and CD spectral data of the four isomers are listed in Tables 2 and 3 respectively.

Infrared Spectrum. The infrared spectrum of the A isomer is slightly different from that of B in shape and position, but it is difficult to assign their configurations on the basis of the infrared spectrum alone. Some characteristic bands are listed in Table 4.

PMR Spectrum. As the *facial* isomer has a threefold axis and three equivalent chelate rings, two PMR signals due to the equatorial and axial methyl groups are expected to appear in the methyl region. On the other hand, the *mer* isomer, which has neither equivalent chelate rings nor an axis of rotation, should show more complicated methyl signals, consisting of up to six peaks. Figure 5 shows the signals observed for the A and B isomers. For the B isomer, only two peaks ($\tau=8.48$, 8.73 ppm) are found, with the area ratio 1 : 1. The peak in the higher field is attributed to the axial methyl group, since the axial proton of the methylene group was found to show signals in a higher field than the equatorial one as a result of the larger shielding by the central metal for $[M(en)_3]^{3+}$ and $[M(l\text{-pn})_3]^{3+}$, where M is Ru(II), Rh(III), Co(III), or Pt(IV).[6] The complicated signals observed for the A isomer at 60 MHz were resolved into five peaks ($\tau=8.44$, 8.58, 8.68, 8.74, 8.77 ppm) at 100 MHz, with the intensity ratio of 1 : 2 : 1 : 1 : 1 suggesting that the A isomer was the *mer* isomer (Fig. 5). MacDermott[2] reported that no difference was observed for two geometrical isomers of *Δ*-$[Co(l\text{-pn})_3]^{3+}$ at 60 MHz, but recently Sudmeier *et al.*[7] have measured the 251 MHz PMR spectrum by the Co-59 decoupling technique and have found a fine structure

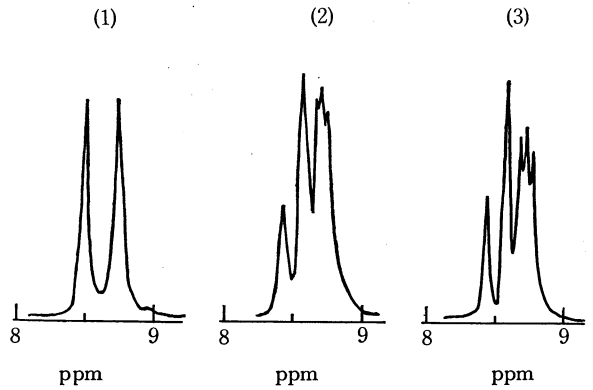


Fig. 5. PMR spectra of (1) the isomer B (60 MHz), (2) the isomer A (60 MHz) and (3) the isomer A (100 MHz) in DMSO-d_6 with TMS as an internal reference.

attributable to nonequivalent propylenediamine rings arising from the presence of geometrical isomers.

Assignment of the Structures. The configurations of the isomers isolated were assigned by means of the formation ratio and the CD and PMR spectra. The relationship between the absolute configuration and the CD spectrum of the tris(diamine)cobalt(III) complexes has been well established[8]; the complex which shows a major positive CD band in the region of the octahedral $^1T_{1g}\leftarrow{}^1A_{1g}$ absorption has the *Λ* configuration in terms of the IUPAC nomenclature. Further, the statistical formation ratio of the *mer* isomer to the *facial* isomer should be 3 : 1 under equilibrium conditions. Thus, the formation ratio, 3 : 1, actually found for the A and B isomers, both of which show a major positive CD band in the first absorption region, indicates that the A isomer is *Λ-mer* and B isomer *Λ-facial*. Similarly, the C and D isomers were identified as *Δ-mer* and *Δ-facial* respectively. The PMR spectral results support these assignments, too. The structure and the absolute configuration of the D isomer was determined by X-ray analysis[9] to be *Δ-facial* with three *lel* chelate rings, confirming the structures proposed above.

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8) A. J. McCaffery and S. F. Mason, *Mol. Phys.*, **6**, 359 (1963).
9) Private communication of Professor Y. Saito, University of Tokyo. A detailed report will be published in *Acta Crystallogr.*