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Preparation and Stereochemistry of Cobalt(III) Complexes Containing *N*-Methylbis(2-aminoethyl)amine

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Seven new cobalt(III) complexes containing *N*-methylbis(2-aminoethyl)amine (4-methyldiethylenetriamine, abbreviated as dema) were prepared and their structures were determined by electronic, circular dichroism, and PMR spectroscopy. For the mixed $[\mathrm{Co(dien)(dema)}]^{3+}$ complex(dien=diethylenetriamine), three geometric isomers, *s-fac*, *u-fac*, and *mer* were isolated. The $[\mathrm{Co(dema)_2}]^{3+}$ complex formed only *s-fac* isomer. A conformational analysis was carried out to compare the stability of these geometric isomers.

Recently three geometric isomers of $[\mathrm{Co(dien)_2}]^{3+}$ (dien=diethylenetriamine) were isolated, and the *u-fac* and the *mer* isomers were resolved into optical antipodes.[1,2] The formation ratio in an equilibrium mixture of the bromides (25 °C),[1] *s-fac*: *u-fac*: *mer*= 7: 30: 63 indicates that the *mer* arrangement is preferred over the *fac* one. The absolute configuration of the $(+)_{589}$-*u-fac* isomer assigned on the basis of the circular dichroism spectrum agreed with that determined by X-ray work.[3] For the *mer* isomer, however, the relationship between the circular dichroism spectrum and the absolute configuration is not clear yet.

The same isomerism is expected for the complex ions, $[\mathrm{Co(dien)(dema)}]^{3+}$ (dema=*N*-methylbis(2-aminoethyl)amine, 4-methyldiethylenetriamine) and $[\mathrm{Co(dema)_2}]^{3+}$. Molecular model studies indicate that the *mer* and the *u-fac* isomers of these complexes involve considerable steric interactions between the methyl group and its surroundings. Accordingly, the distribution of isomers in these complexes will differ from that in $[\mathrm{Co(dien)_2}]^{3+}$. It will also be interesting to see how such steric interactions are reflected on the absorption and circular dichroism spectra.

Experimental

Ligands. *N*-Methylbis(2-aminoethyl)amine (dema) and its hydrochloride(dema·3HCl) were prepared by the method of Nakajima *et al.*[4] Diethylenetriamine(dien) was obtained from Tokyo Kasei Co., and used without further purification.

$[Co(NO_2)_3(dema)]$ and $[CoCl_2(H_2O)(dema)]Cl\cdot 0.5H_2O$. $[\mathrm{Co(NO_2)_3(dema)}]$ was prepared from $\mathrm{Co(NO_3)_2\cdot 6H_2O}$, $\mathrm{NaNO_2}$, and dema by a method similar to that for $[\mathrm{Co(NO_2)_3(dien)}]$,[5] and recrystallized from water containing a small amount of $\mathrm{NaNO_2}$ and a few drops of acetic acid . Orange needle crystals were filtered off, washed with water and air dried, 60% yield. Found: C, 18.93; H, 4.64; N, 26.71%. Calcd for $\mathrm{CoC_5H_{15}N_6O_6}$=$[\mathrm{Co(NO_2)_3(dema)}]$: C, 19.12; H, 4.81; N, 26.75%.

$[\mathrm{Co(NO_2)_3(dema)}]$(6.8 g, 22 mmol) was gently heated with 70 cm^3 of concd HCl until the evolution of nitrogen dioxide ceased. Fine blue crystals which formed on standing the resulting solution overnight at room temperature were filtered off and washed with acetone, 75% yield. Found: C, 19.22; H, 6.13; N, 13.08; $\mathrm{H_2O}$, 8.92%. Calcd for $\mathrm{CoC_5H_{18}N_3O_{0.5}Cl_3}$=$[\mathrm{CoCl_2(H_2O)(dema)}]\mathrm{Cl\cdot 0.5H_2O}$: C, 19.39; H, 5.86; N, 13.58; $\mathrm{H_2O}$, 8.74%.

s-fac-*$[Co(dien)(dema)]Cl_3\cdot H_2O$(Isomer A).* To a solution of $\mathrm{CoCl_2\cdot 6H_2O}$(0.6 g, 2.5 mmol) in 10 cm^3 of water were added a solution of dema (0.4 g, 3.5 mmol) and dien (0.35 g, 3.5 mmol) in 10 cm^3 of water, and active charcoal (0.3 g). The mixture was aerated for 6 h at room temperature, and filtered to remove the charcoal. The resulting orange filtrate was diluted with about 1 dm^3 of water and passed through an SP-Sephadex column ($\phi 2.5\times 4$ cm). A small portion of the SP-Sephadex charged with the product was poured on the top of the adsorbent layer of an SP-Sephadex column ($\phi 2.7\times 120$ cm) and the adsorbed complexes were eluted with a 0.2 M aqueous solution of $\mathrm{Na_2SO_4}$. Three separate bands were obtained. The first band was *s-fac*-$[\mathrm{Co(dien)_2}]^{3+}$, but the second and the third bands were mixtures of *u-fac*-$[\mathrm{Co(dien)_2}]^{3+}$ and *s-fac*-$[\mathrm{Co(dien)(dema)}]^{3+}$, and *mer*-$[\mathrm{Co(dien)_2}]^{3+}$ and *s-fac*-$[\mathrm{Co(dema)_2}]^{3+}$, respectively. The effluent of the second band was diluted with water and reloaded on an SP-Sephadex column, and the adsorbed band was eluted with a 0.15 M sodium $(+)_{589}$-tartratoantimonate(III) solution. Three separate bands, $\mathrm{II_A}$, $\mathrm{II_B}$, and $\mathrm{II_C}$ which eluted in this order were $(+)_{589}$-*u-fac*-$[\mathrm{Co(dien)_2}]^{3+}$, $(-)_{589}$-*u-fac*-$[\mathrm{Co(dien)_2}]^{3+}$, and *s-fac*-$[\mathrm{Co(dien)(dema)}]^{3+}$, respectively. The third band was rechromatographed by a method similar to that for the second band. The column gave three separate bands, $\mathrm{III_A}$, $\mathrm{III_B}$, and $\mathrm{III_C}$ in the order of elution, which were $(+)_{589}$-*mer*-$[\mathrm{Co(dien)_2}]^{3+}$, $(-)_{589}$-*mer*-$[\mathrm{Co(dien)_2}]^{3+}$, and *s-fac*-$[\mathrm{Co(dema)_2}]^{3+}$, respectively. The formation ratio, *s-fac*-$[\mathrm{Co(dien)_2}]^{3+}$: *u-fac*-$[\mathrm{Co(dien)_2}]^{3+}$: *mer*-$[\mathrm{Co(dien)_2}]^{3+}$: *s-fac*-$[\mathrm{Co(dien)(dema)}]^{3+}$: *s-fac*-$[\mathrm{Co(dema)_2}]^{3+}$ was about 1: 4: 15: 6: 5. The effluent containing *s-fac*-$[\mathrm{Co(dien)(dema)}]^{3+}$ was diluted with water and poured again on an SP-Sephadex column ($\phi 1.5\times 3$ cm), the column was washed with a large amount of 10^{-2} M HCl, and then the adsorbed complex was eluted with 1.0 M HCl. Orange crystals were obtained by evaporating the effluent to almost dryness in a vacuum desiccator over NaOH and $\mathrm{P_2O_5}$. Found: C, 26.41; H, 7.40; N, 20.98%. Calcd for $\mathrm{CoC_9H_{30}N_6OCl_3}$=*s-fac*-$[\mathrm{Co(dien)(dema)}]\mathrm{Cl_3\cdot H_2O}$: C, 26.78; H, 7.49; N, 20.82%.

u-fac-*$[Co(dien)(dema)]^{3+}$(Isomer B).* An aqueous solution (50 cm^3) of dien·3HCl(0.63 g, 3 mmol) neutralized with $\mathrm{NaHCO_3}$ (0.75 g, 9 mmol) was added to a solution of $[\mathrm{CoCl_2(H_2O)(dema)}]\mathrm{Cl\cdot 0.5H_2O}$(0.9 g, 3 mmol) in 50 cm^3 of water. The solution was heated at 50 °C for 40 h, and then diluted with 1 dm^3 of water. The solution was poured on an SP-Sephadex column ($\phi 2.5\times 4$ cm), and the adsorbed product was chromatographed by a method similar to that for *s-fac*-$[\mathrm{Co(dien)(dema)}]^{3+}$ with a 0.2 M aqueous aolution of $\mathrm{Na_2SO_4}$. The column gave orange, red-violet, and violet bands in the order of elution. The effluent of the first orange band was diluted with water and reloaded on an SP-Sephadex column, and the adsorbed band was eluted with a 0.2 M sodium $(+)_{589}$-tartrate solution. The column showed three yellow-orange bands. The first, the second, and the third bands in the order of elution were *u-fac*-$[\mathrm{Co(dien)(dema)}]^{3+}$, *s-fac*-$[\mathrm{Co(dien)(dema)}]^{3+}$, and *u-fac*-$[\mathrm{Co(dien)_2}]^{3+}$, respectively. The effluent of *u-fac*-$[Co(dien)(dema)]^{3+}$ was diluted with water and poured again on an SP-Sephadex column ($\phi 1.5 \times 3$ cm), and the adsorbed complex was eluted with a 1.0 M NaCl solution. The complex was isolated as hexacyanocobaltate(III) salt by adding a $K_3[Co(CN)_6]$ solution to the effluent. Found: C, 33.26; H, 6.28; N, 30.74%. Calcd for $Co_2C_{15}H_{34}N_{12}O_3$= *u-fac*-$[Co(dien)(dema)][Co(CN)_6]\cdot 3H_2O$: C, 32.85; H, 6.25; N, 30.64%. The complex hexacyanocobaltate(III) was converted into chloride by use of the anion exchanger, Dowex 1×8 in the chloride form. The complex chloride did not crystallize on the addition of common organic solvents to a concentrate of the chloride solution. Thus, the orange residue obtained by evaporation in a vacuum desiccator was used for measurement.

The complex was resolved by SP-Sephadex column chromatography with a 0.15 M sodium $(+)_{589}$-tartratoantimonate(III) solution as the eluent. The optically active chloride salt was isolated as an orange residue by a method similar to that for the racemic complex chloride.

mer-*$[Co(dien)(dema)]^{3+}$(Isomer C)*. To a suspension of *mer*-$[CoCl_3(dien)]$[6] (2.2 g, 8.2 mmol) in 10 cm^3 of *N,N*-dimethylformamide (DMF) was added dema (1.0 g, 8.5 mmol), and the mixture was stirred for 1 h at 50 °C. The resulting orange solution was diluted to 1 dm^3 with water, and poured on SP-Sephadex. The product adsorbed on SP-Sephadex was similarly chromatographed. By elution with 0.15 M sodium $(+)_{589}$-tartratoantimonate (III), the column gave two pairs of enantiomers, the fast-(very small amount) and the slow-moving bands being $(+)_{589}$- and $(-)_{589}$-*mer*-$[Co(dien)_2]^{3+}$ and $(-)_{490}$- and $(+)_{490}$-*mer*-$[Co(dien)(dema)]^{3+}$, respectively. The optically active *mer*-$[Co(dien)(dema)]^{3+}$ was isolated as hexacyanocobaltate(III) salt by a method similar to that for *u-fac*-$[Co(dien)(dema)]^{3+}$, and the isolated salt was converted into bromide with the anion exchanger, Dowex 1X 8 in the bromide form. The solution of the complex bromide was evaporated to dryness in a vacuum desiccator to give orange crystals. Found: C, 19.30; H, 5.74; N, 14.82%. Calcd for $CoC_9H_{33}N_6Br_3O_{2.5}=(+)_{490}$-*mer*-$[Co(dien)(dema)]Br_3\cdot 2.5H_2O$: C, 19.17; H, 5.90; N, 14.89%. The racemic complex was isolated as perchlorate salt by the following method; the effluents containing $(-)_{490}$- and $(+)_{490}$- isomers were combined, diluted with water, and poured on SP-Sephadex. The adsorbed complex was eluted with a 1.5 M $NaClO_4$ solution and the effluent was concentrated in a vacuum desiccator over P_2O_5 to give orange crystals. Found: C, 17.74; H, 5.21; N, 13.70%. Calcd for $CoC_9H_{32}N_6O_{14}Cl_3$=*mer*-$[Co(dien)(dema)](ClO_4)_3\cdot 2H_2O$: C, 17.62; H, 5.26; N, 13.69%.

s-fac-*$[Co(dema)_2]^{3+}$*. *Method 1*: A solution of dema·3HCl(5.0 g, 22 mmol) in water (20 cm^3) was neutralized with an aqueous solution (10 cm^3) of NaOH (2.4 g, 60 mmol) or Na_2CO_3(3.2 g, 30 mmol). The solution was added to a solution of $CoCl_2\cdot 6H_2O$ (2.38 g, 10 mmol) in water (30 cm^3), and then mixed with active charcoal (0.5 g). The mixture was aerated for 12—120 h at room temperature.

Method 2: To a solution of $CoCl_2\cdot 6H_2O$ (0.24 g, 1 mmol) in 50 cm^3 of water were added a solution of $Na_3PO_4\cdot 12H_2O$ (1.9 g, 5 mmol) and dema·3HCl (0.46 g, 2 mmol) in water (10 cm^3), and active charcoal (0.2 g). The cobalt ions were oxidized by bubbling a stream of air through the solution at room temperature for 22 h. The addition of phosphate is known to change the distribution of isomers in the complex formation of $[Co(dien)_2]^{3+}$.[7]

Method 3: To a dimethyl sulfoxide (DMSO) solution (20 cm^3) containing $Co(NO_3)_2\cdot 6H_2O$(0.29 g, 1 mmol) and dema·3HCl(0.23 g, 1 mmol) were added a solution of dema(0.29 g, 2.5 mmol) in DMSO (10 cm^3), and active charcoal (0.2 g). The oxidation of cobalt ions was carried out under the same conditions as that for Method 2.

Method 4: A solution of dema·3HCl (0.91 g, 4 mmol) in 10 cm^3 of water was neutralized with Na_2CO_3 (0.64 g, 6 mmol). To this solution were added a solution of $[Co(H_2O)(NH_3)_5](ClO_4)_3$(0.46 g, 1 mmol) in water (20 cm^3), and active charcoal (0.2 g). The mixture was heated at 70—80 °C for 2 h.

Method 5: To a solution of $[Co(H_2O)(NH_3)_5](ClO_4)_3$(0.92 g, 2 mmol) in 20 cm^3 of DMSO was added a DMSO solution (10 cm^3) of dema (0.8 g, 7 mmol). The solution was heated at 85 °C for 15 min.

Method 6: To a solution of dema·3HCl (0.68 g, 3 mmol) and sodium methoxide (0.41 g, 7.5 mmol) in methanol (12 cm^3) was added a solution of *trans*-$[CoCl_2(py)_4]Cl\cdot 6H_2O$[8] (0.59 g, 1 mmol) in methanol (8 cm^3). The reaction took place immediately to give orange precipitate.

Method 8: This method was the same as Method 7 except that pyridine was used as the solvent instead of methanol.

Method 9: To an ice-cold, stirred solution of $K_3[Co(CO_3)_3]$[9] (2.1 mmol) in water (5 cm^3) was added dropwise a solution of dema·3HCl (1.0 g, 4.4 mmol) in water (5 cm^3). The mixture was heated at 70—80 °C for 6 h until the color of the solution became red. The solution was mixted with acetic acid (50%, 15 cm^3) and heated further 2 h.

Method 10: To a solution of dema (2 g, 17 mmol) in 10 cm^3 of DMF was added $[CoCl_2(H_2O)(dema)]Cl\cdot 0.5H_2O$ (0.8 g, 2.7 mmol). The mixture was heated at 50 °C for 2 h.

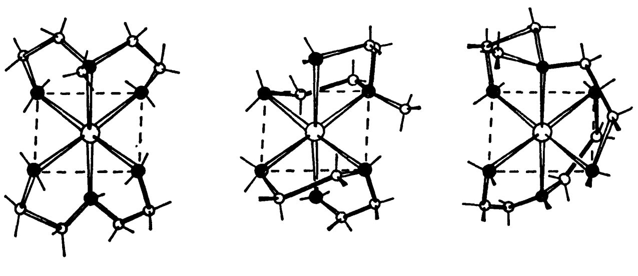
Method 11: This method was the same as Method 1 except that the aeration was carried out at 80 °C for 7 h.

The reaction mixtures were filtered to remove the charcoal if necessary, diluted with water, and then the pH of the solutions were adjusted to 4—6 with HCl. A small amount of each solution was applied to SP-Sephadex column ($\phi 2.7 \times 120$ cm) chromatography. The eluents used were 0.2 M sodium sulfate, 0.2 M sodium $(+)_{589}$-tartrate, or 0.15 M sodium $(+)_{589}$-tartratoantimonate(III) solutions. All the preparative methods except for Method 11 gave only one isomer, *s-fac*-$[Co(dema)_2]^{3+}$. No indication for the formation of other isomers was found. The complex was isolated as perchlorate salt by a method similar to that for *mer*-$[Co(dien)(dema)](ClO_4)_3\cdot 2H_2O$. Found: C, 20.04; H, 5.00; N, 14.12%. Calcd for $CoC_{10}H_{31}N_6O_{12.5}Cl_3$=*s-fac*-$[Co(dema)_2](ClO_4)_3\cdot 0.5H_2O$: C, 20.00; H, 5.20; N, 13.99%. The solution obtained from Method 11 was chromatographed in a manner similar to those for Method 1—10. By elution with a 0.2 M Na_2SO_4 solution, the column gave four yellow-orange bands. The first small band was *s-fac*-$[Co(dien)(dema)]^{3+}$ which may be a demethylated product of *s-fac*-$[Co(dema)_2]^{3+}$, and the second main band was *s-fac*-$[Co(dema)_2]^{3+}$. Complexes obtained from the third and the fourth bands gave analytical results which do not correspond to the dien or dema complexes, and were not characterized.

Measurements. Absorption and diffuse reflectance spectra were recorded on a Hitachi 323 spectrophotometer, and circular dichroism spectra on a JASCO model J-20 spectropolarimeter. PMR spectra were recorded on a JEOL PMX-60 spectrometer at 60 MHz in DMSO-d_6 with TMS as the internal reference.

Results and Discussion

Preparation and Characterization of the Isomers. *(i) $[Co(NO_2)_3(dema)]$, $[CoCl_2(H_2O)(dema)]^+$, and $[CoCl_3(dema)]$*: The $[Co(NO_2)_3(dien)]$ complex has been determined to be *mer* configuration by X-ray analysis.[10] By heating this complex with concd hydrochloric acid, brown crystals of $[\mathrm{CoCl_3(dien)}]$ are obtained.[7] It gives only *mer* isomer of $[\mathrm{Co(dien)(dema)}]^{3+}$ by reacting with dema in DMF. On the other hand, the reaction of $[\mathrm{Co(NO_2)_3(dema)}]$ with concd hydrochloric acid yields blue crystals of $[\mathrm{CoCl_2(H_2O)(dema)}]\mathrm{Cl\cdot 0.5H_2O}$, which turn green $[\mathrm{CoCl_3(dema)}]$ by heating at 110 °C for 1 h *in vacuo*. These chlorodema complexes give only *s-fac*-$[\mathrm{Co(dema)_2}]^{3+}$ by the reaction with dema. These results and the diffuse reflectance spectra of the tri-chloro complexes (*vide post*) indicate that the dien and the dema ligands in the present nitro and chloro complexes have *mer* and *fac* configurations, respectively. Two geometric isomers are possible for *fac*-$[\mathrm{CoCl_2(H_2O)(dema)}]^{+}$. However, the structure of the present blue complex could not be assigned by PMR and absorption spectroscopy.



(a) *s-fac* (b) *u-fac* (c) *mer*

Fig. 1. Three geometric isomers of $[\mathrm{Co(dien)(dema)}]^{3+}$.

(ii) $[\mathit{Co(dien)(dema)}]^{3+}$: As Fig. 1 shows, the *s-fac* isomer is achiral, while both the *u-fac* and the *mer* isomers are chiral and exist each in a pair of enantiomers. The *mer* isomer is expected to be optically stable only in acidic solution as has been observed for *mer*-$[\mathrm{Co(dien)_2}]^{3+}$.[1,2] The isomer A can be assigned to the *s-fac* isomer, since it is not resolved, while the other two isomers (the isomers B and C) are completely resolved. The resolved isomer C loses rapidly its optical activity in alkaline solution, but the isomer B is optically stable under the same condition. Thus the isomers B and C are assigned to the *u-fac* and the *mer* isomers, respectively. As described in Experimental part, only the *s-fac* isomer of $[\mathrm{Co(dien)(dema)}]^{3+}$ was isolated from the product obtained by the reaction in the presence of active charcoal, although the product contained three isomers of $[\mathrm{Co(dien)_2}]^{3+}$ and *s-fac*-$[\mathrm{Co(dema)_2}]^{3+}$. Strain energy minimization calculation reveals that the *u-fac* and the *mer* isomers are less stable than the *s-fac* isomer by 22.1 and 6.1 kJ·mol^{-1}, respectively (*vide post*).

The *u-fac* isomer was obtained by the reaction of *fac*-$[\mathrm{CoCl_2(H_2O)(dema)}]\mathrm{Cl\cdot 0.5H_2O}$ with dien in water without the addition of active charcoal. The *mer* isomer was prepared similarly from *mer*-$[\mathrm{CoCl_3(dien)}]$ and dema in DMF, as stated previously. The triamine ligands in the starting complexes seem to retain the arrangement in these substitution reactions.

(iii) $[\mathit{Co(dema)_2}]^{3+}$: All the preparative methods give a single geometric isomer as evidenced by column chromatography. The PMR spectrum of $[\mathrm{Co(dema)_2}](\mathrm{ClO_4})_3\cdot 0.5\mathrm{H_2O}$ in DMSO-d_6 exhibits only one kind of the $\mathrm{NH_2}$ group, (δ=5.1 ppm). In the *s-fac* isomer, the $\mathrm{NH_2}$ groups should be equivalent, while the other two isomers have two nonequivalent sets of $\mathrm{NH_2}$ groups (Fig. 1). Thus, the complex can be assigned to the *s-fac* isomer. Conformational analysis also indicates that the *s-fac* isomer is the most stable (*vide post*).

Very recently, Searle and Larsen[11] reported the PMR data for the *u-fac* isomer, but did not describe the preparative method.

Absorption and Circular Dichroism Spectra. Figure 2 and Table 1 compare the absorption spectra of the *s-fac* isomers of $[\mathrm{Co(dema)_2}]^{3+}$, $[\mathrm{Co(dien)(dema)}]^{3+}$, and $[\mathrm{Co(dien)_2}]^{3+}$. All of the absorption bands shift to longer wavelengths as the number of the dema ligand increases. A similar shift is observed for a series of complexes of the type $[\mathrm{Co(en)}_x(N\text{-}\mathrm{meen})_{3-x}]^{3+}$ (x=0—3, N-meen=N-methylethylenediamine).[12] The differences in the absorption maxima of the first absorption bands amount to 480 cm^{-1} between $[\mathrm{Co(dien)_2}]^{3+}$ and $[\mathrm{Co(dien)(dema)}]^{3+}$ and 490 cm^{-1} between $[\mathrm{Co(dien)(dema)}]^{3+}$ and $[\mathrm{Co(dema)_2}]^{3+}$. Therefore, it is concluded that dema is located at a lower position than dien in the spectrochemical series. Both *s-fac*-[Co-

Table 1. Absorption and CD spectral data

Complex	Absorption		CD	
	$\tilde{\nu}$/cm^{-1}	log ε	$\tilde{\nu}$/cm^{-1}	$\Delta\varepsilon$
s-fac-$[\mathrm{Co(dien)_2}]^{+}$	21760	1.84		
	29900	1.80		
	47200	4.35		
$(+)_{589}$-*u-fac*-$[\mathrm{Co(dien))_2}]^{3+}$	21370	1.99	19900	+0.98
			22500	−0.84
	29500	1.97	29900	+0.37
	46200	4.35	44400	−9.0
			50700	+7.4
$(+)_{589}$-*mer*-$[\mathrm{Co(dien)_2}]^{3+}$	21460	2.17	19500	+0.096
			21900	−0.18
	29200	2.05	27800	−0.014
			30700	+0.057
	44400	4.32	45500	+0.26
s-fac-$[\mathrm{Co(dien)(dema)}]^{3+}$	21280	1.90		
	29600	1.86		
	45500	4.32		
$(+)_{589}$-*u-fac*-$[\mathrm{Co(dien)(dema)}]^{3+}$	20750	2.06	19840	+1.02
			22270	−0.023
	29100	1.99	27200	+0.30
	44500	4.32	38600	+1.0
			43500	−6.7
			48500	+6.6
$(-)_{490}$-*mer*-$[\mathrm{Co(dien)(dema)}]^{3+}$	20790	2.17	19120	+0.083
			21410	−0.19
	28700	2.13	29000	+0.080
	43300	4.25	43000	+0.36
			49000	−0.86
s-fac-$[\mathrm{Co(dema)_2}]^{3+}$	20790	1.90		
	29400	1.89		
	44600	4.25		
mer-$[\mathrm{Co(NO_2)_3(dien)}]$	23300	2.56		
	29700	3.80		
	39700	4.41		
fac-$[\mathrm{Co(NO_2)_3(dema)}]$	22600	2.54		
	29500	3.83		
	39200	4.39		

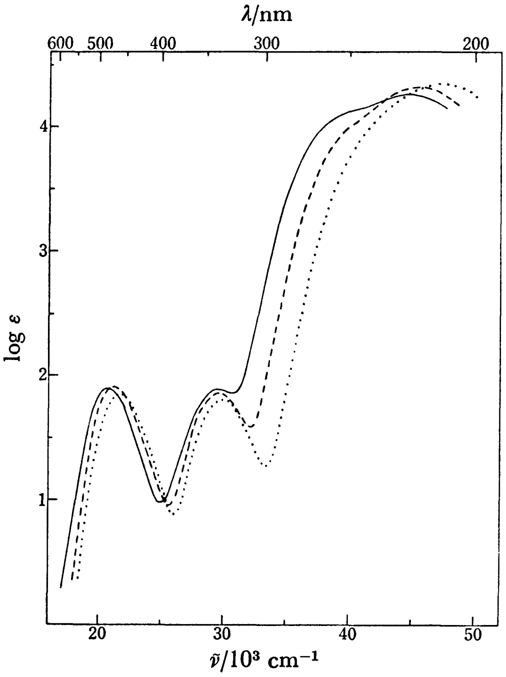


Fig. 2. Absorption spectra of the *s-fac* isomers of [Co(dema)$_2$]$^{3+}$ (——), [Co(dien)(dema)]$^{3+}$ (– – –), and [Co(dien)$_2$]$^{3+}$ (······) in water.

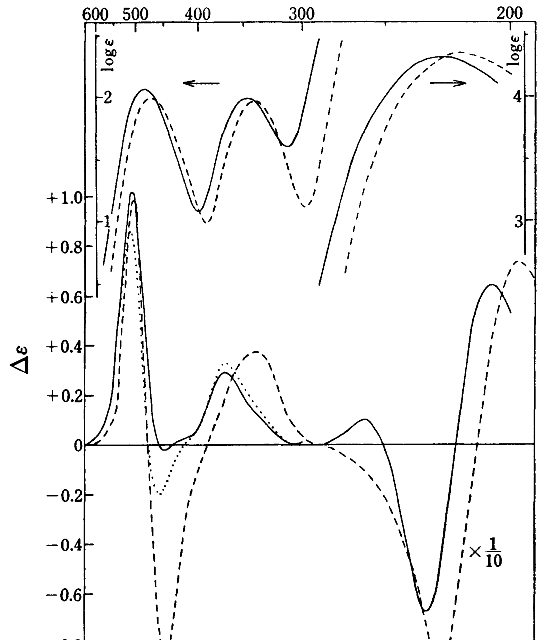


Fig. 3. Absorption and CD spectra of $(+)_{589}$-*u-fac*-[Co(dien)(dema)]$^{3+}$ in water (——) and CD spectrum in 0.2 M Na_2SO_4 (······). Absorption and CD spectra of $(+)_{589}$-*u-fac*-[Co(dien)$_2$]$^{3+}$ in water (– – –).

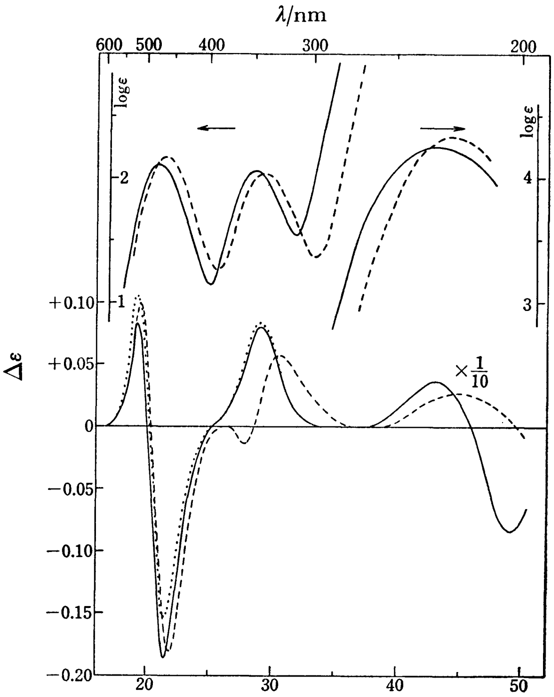


Fig. 4. Absorption and CD spectra of $(-)_{490}$-*mer*-[Co(dien)(dema)]$^{3+}$ in 10^{-2} M HCl (——) and CD spectrum in 0.2 M Na_2SO_4–10^{-2} M HCl (······). Absorption and CD spectra of $(+)_{589}$-*mer*-[Co(dien)$_2$]$^{3+}$ in 10^{-2} M HCl (– – –).

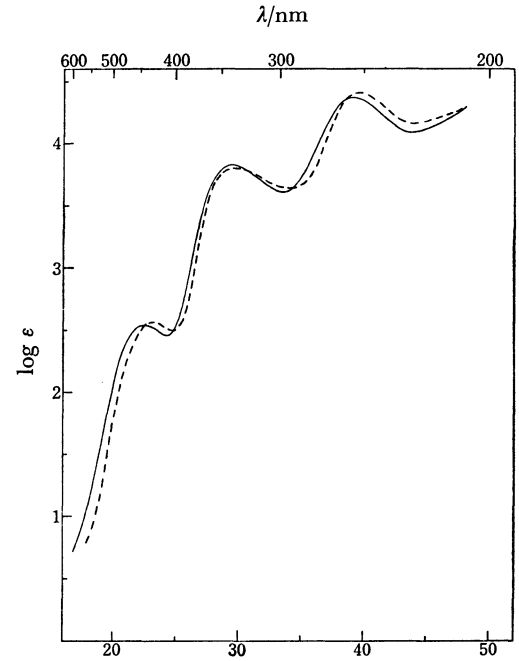


Fig. 5. Absorption spectra of *mer*-[Co(NO$_2$)$_3$(dien)] (– – –) and *fac*-[Co(NO$_2$)$_3$(dema)] (——) in water.

(dien)(dema)]$^{3+}$ and *s-fac*-[Co(dema)$_2$]$^{3+}$ exhibit shoulders at a longer wavelength side of the charge transfer bands. These shoulders may correspond to the charge transfer transitions from the tertiary nitrogen atom of the dema ligand to the central cobalt ion. The absorption bands of the *u-fac* and the *mer* isomers of [Co(dien)(dema)]$^{3+}$ are also at a longer wavelength side than those of the corresponding isomers of [Co(dien)$_2$]$^{3+}$

(Figs. 3 and 4, and Table 1). The first absorption bands of the isomers of $[Co(dien)(dema)]^{3+}$ shift to longer wavelengths in the order of *s-fac*, *mer*, and *u-fac* isomers, the same order being observed in the isomers of $[Co(dien)_2]^{3+}$.1)

Figure 5 shows the absorption spectra of *mer*-$[Co(NO_2)_3(dien)]$ and $[Co(NO_2)_3(dema)]$ which was assigned to the *fac* configuration as stated previously. The former has a pair of nitrite ions in the *trans* positions. It is known that the so-called nitro specific band ($\approx$30000 cm^{-1}) of a *trans*-dinitrocobalt(III) complex is located at a longer wavelength than that of the corresponding *cis* complex. However, the present nitro complexes give their nitro specific bands at nearly the same position.

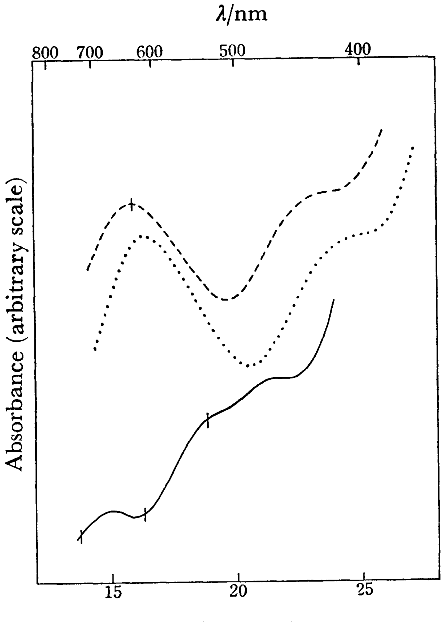


Fig. 6. Diffuse reflectance spectra of *mer*-$[CoCl_3(dien)]$ (——), *fac*-$[CoCl_3(dema)]$ (----), and *fac*-$[CoCl_2(H_2O)(dema)]Cl\cdot 0.5H_2O$ (······). Short vertical lines show the calculated band positions.

Figure 6 compares the diffuse reflectance spectra of $[CoCl_3(dien)]$ and $[CoCl_3(dema)]$, which have been assigned previously to the *mer* and the *fac* configurations, respectively. These tri-chloro complexes are hardly soluble in common organic solvents and aquate rapidly in water. From Yamatera's theory,13) the first absorption band of *mer*-$[CoCl_3(dien)]$ is expected to split into three components, and their positions can also be predicted. Since the first absorption maximum (21.5×10^3 cm^{-1}) of *mer*-$[Co(dien)_2]^{3+}$ is at nearly the same position as that of $[Co(en)_3]^{3+}$ (21.4×10^3 cm^{-1}), the values of parameters, $\delta(N)$ and $\delta(Cl)$ for *mer*-$[CoCl_3(dien)]$ may be approximated to those obtained from $[Co(en)_3]^{3+}$ and *trans*-$[CoCl_2(en)_2]^{+}$14) (21.6, 16.2×10^3 cm^{-1}). The predicted positions of the three components of *mer*-$[CoCl_3(dien)]$ are 18.85, 16.3, and 13.75×10^3 cm^{-1}. On the other hand, no splitting is expected for the first absorption band of *fac*-$[CoCl_3(dema)]$. The first absorption band of *s-fac*-$[Co(dema)_2]^{3+}$ (20.8×10^3 cm^{-1}) is at nearly the same position as that of $[Co(NH_3)_6]^{3+}$ (21.0×10^3 cm^{-1}). Thus, the first absorption band of *fac*-$[CoCl_3(dema)]$ is similarly predicted at *ca.* 15.9×10^3 cm^{-1} with reference to the maximum positions of *trans*-$[CoCl_2(NH_3)_4]^{+}$15) (21.0 and 15.9×10^3 cm^{-1}). The predicted values for both the tri-chloro complexes satisfy the observed spectra as marked on the curves in Fig. 6. These results will support the previous assignment for the structures of *mer*-$[CoCl_3(dien)]$ and *fac*-$[CoCl_3(dema)]$. The first absorption band of *fac*-$[CoCl_2(H_2O)(dema)]Cl\cdot 0.5H_2O$ is at a shorter wavelength (610 nm) than that of *fac*-$[CoCl_3(dema)]$ (630 nm) in accordance with the order of the spectrochemical series of H_2O and Cl^-, indicating that the water molecule coordinates to the cobalt ion.

In Fig. 3 the absorption and CD spectra of $(+)_{589}$-*u-fac*-$[Co(dien)(dema)]^{3+}$ are shown. It exhibits a CD spectrum similar to that of Λ-$(+)_{589}$-*u-fac*-$[Co(dien)_2]^{3+}$3) over the entire region. The effect of sulfate ions on the CD spectrum of $(+)_{589}$-*u-fac*-$[Co(dien)(dema)]^{3+}$ is also similar to that of the corresponding bis-dien complex. Thus, the absolute configuration of $(+)_{589}$-*u-fac*-$[Co(dien)(dema)]^{3+}$ can be assingned to Λ.

As Fig. 1 shows, *mer*-$[Co(dien)(dema)]^{3+}$ has an equal number of Δ and Λ ring-pairs, and of δ and λ conformers. Hence, the chiral contributions from the configurational and the conformational effects may be canceled out as in the case of *mer*-$[Co(dien)_2]^{3+}$. The chirality in the *mer*-$[Co(dien)(dema)]^{3+}$ isomer should come from the stereochemical relationship between the N–H bond of the secondary nitrogen atom in the dien ligand and the N-CH_3 bond in the dema ligand. The CD spectrum of $(-)_{490}$-*mer*-$[Co(dien)(dema)]^{3+}$ is shown in Fig. 4. The pattern and magnitude of the CD spectrum of this isomer, and the changes in the CD band area on the addition of sulfate are all similar to those of $(+)_{589}$-*mer*-$[Co(dien)_2]^{3+}$. Therefore, it can be concluded that these two isomers have the same absolute configuration. However, the relationship between the CD sign and the absolute configuration for complexes of this type still remains unknown.

The active *mer*-$[Co(dien)(dema)]^{3+}$ isomer is optically stable over one year in acidic water (*ca.* pH 2) at room temperature (*ca.* 25 °C), but racemizes immediately on raising the pH to 12 by adding a NaOH solution.

Conformational Analysis. The strain energies of the isomers of $[Co(dien)(dema)]^{3+}$ and $[Co(dema)_2]^{3+}$ were calculated by the previously reported method,16) the force field in which includes the contributions from bond stretching, nonbonded interactions, angle bending, and tortional potentials. The initial molecular structures of the isomers were the same as those of the final results obtained previously for the corresponding $[Co(dien)_2]^{3+}$ isomers,16) except that the N–C(H_3) bond of 1.5 Å was taken for the dema ligand instead of the N–H (secondary amine) bond of dien. When the dema ligand coordinates to the Co(III) ion, the Co–N(CH_3) (tertiary amine) distance lengthens (1.99—2.02 Å) compared with the Co–N(H) (secondary amine) distance (1.94—1.97 Å), and the ∠CoNC (of the methyl group) angle becomes much larger (117—120°) than the normal tetrahedral angle. Similar results are also obtained for the

TABLE 2. FINAL ENERGY TERMS FOR THE ISOMERS OF $[Co(dien)(dema)]^{3+}$ AND $[Co(dema)_2]^{3+}$

Isomer	Bond	Nonbond	Angle	Torsion	Total
$[Co(dien)(dema)]^{3+}$					
s-fac	6.42	34.10	16.28	31.17	89.58 kJ·mol^{-1}
u-fac[a]	8.74	41.29	20.22	41.39	111.64
mer	7.62	35.64	25.77	26.63	95.65
$[Co(dema)_2]^{3+}$					
s-fac	11.16	47.08	23.91	31.37	113.53
u-fac[a]	14.06	51.86	36.90	32.55	134.38
mer	11.97	53.09	27.71	30.79	123.56

a) This isomer corresponds to the *u-fac*-1 isomer in the preceding paper.[16] The *u-fac*-2 isomer has the more strained structure.

N-methylethylenediamine[17] and sarcosinato[18] complexes of Co(III). Table 2 shows the minimized energy terms of all the isomers of $[Co(dien)(dema)]^{3+}$ and $[Co(dema)_2]^{3+}$. In contrast to the case of $[Co(dien)_2]^{3+}$, of which the energies of the isomers are calculated to be *mer*≲*s-fac*≲*u-fac*,[16] both the dema complexes have the lowest and the highest energies in the *s-fac* and the *u-fac* isomers, respectively. As stated in Experimental part, the reaction of $CoCl_2 \cdot 6H_2O$ with a mixture of dien and dema (1:1) in the presence of active charcoal produced only the *s-fac* isomers of $[Co(dien)(dema)]^{3+}$ and $[Co(dema)_2]^{3+}$, together with the three isomers of the bis-dien complex. The other isomers of $[Co(dien)(dema)]^{3+}$ were not detected in SP-Sephadex column chromatography, although the energy difference between the *s-fac* and the *mer* isomers was calculated to be 6.1 kJ·mol^{-1}. The *u-fac* and the *mer* isomers of $[Co(dien)(dema)]^{3+}$ were prepared from *fac*-$[CoCl_2(H_2O)(dema)]^+$ and *mer*-$[CoCl_3(dien)]$, respectively in the absence of active charcoal. All the preparative methods for $[Co(dema)_2]^{3+}$ gave always only the *s-fac* isomer. If the calculated energy differences among the isomers of this complex were correct, the formation of other isomers than the *s-fac* would almost be zero. Thus, the experimental results agree with those obtained by the energy minimization calculation; each complex of $[Co(dien)(dema)]^{3+}$ and $[Co(dema)_2]^{3+}$ is the most stable in the *s-fac* isomer.

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