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Isomerism of the Metal Complexes containing Multidentate Ligands. I. Geometric and Optical Isomers of the Bis(diethylenetriamine)-cobalt(III) Ion[1]

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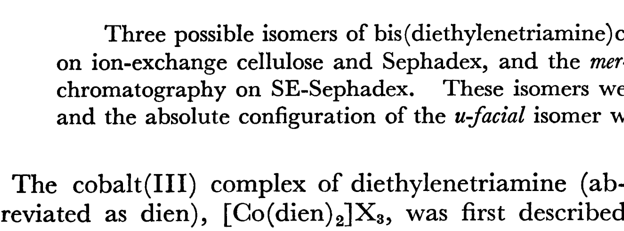
Three possible isomers of bis(diethylenetriamine)cobalt(III) halide were isolated by column chromatography on ion-exchange cellulose and Sephadex, and the *mer-* and *u-facial* isomers were completely resolved by column chromatography on SE-Sephadex. These isomers were studied by electronic, infrared, and PMR spectroscopy, and the absolute configuration of the *u-facial* isomer was assigned on the basis of the circular dichroism spectrum.

The cobalt(III) complex of diethylenetriamine (abbreviated as dien), $[Co(dien)_2]X_3$, was first described by Mann[2] in 1934. Later Brigando *et al.*[3] and also Schmidtke[4] measured the absorption spectrum in the visible and ultraviolet regions, and Basolo *et al.*[5] determined the rate of proton exchange of this complex. These authors, however, did not refer to the possible isomers of this complex, and it is not certain which isomer was used for these investigations. The complex, $[Co(dien)_2]X_3$ can exist in three geometric isomers, as is shown in Fig. 1; the isomerism has been discussed by several authors,[6—10] but the isomers have never been isolated and characterized. In a previous paper[11] we have reported the resolution of one of the isomers of this complex by column chromatography on P-cellulose. The details of the isolation and characterization of all three isomers will be described in the present paper.



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

Fig. 1. Three geometric isomers of $[Co(dien)_2]^{3+}$. The hydrogen atoms of the $-CH_2-$ groups are not shown. The figure 1 (c) represents the configuration of the $(+)_{589}$-*u-facial* isomer. The configuration of $(+)_{589}$-$[Co(penten)]^{3+}$ is the same with 1(c), the N_1 and N_2 atoms being linked by an ethylene group.

Experimental

1.1. Measurements. All the measurements were carried out at 25°C. The electronic absorption, optical rotatory dispersion (ORD), and circular dichroism (CD) spectra were measured by means of a JASCO ORD/UV-5 and a JASCO J-20 spectrometer, using quartz cells 1, 5, and 10 mm thick. The intensities of the ORD and CD spectra were checked using those of $(+)_{589}$-$[Co(en)_3]Br_3 \cdot H_2O$, $[M]^{25}_{589}=602°$,[12] and $\Delta\varepsilon_{490}=+1.89$[13,14] as references. The infrared spectrum (4000—650 cm^{-1}) was measured with a JASCO-402G infrared spectrophotometer by using Nujol and hexachlorobutadiene mulls, and the far-infrared spectrum (700—200 cm^{-1}), with a Hitachi EPI-L spectrophotometer by using Nujol mulls. The PMR spectrum in deuterated dimethylsulfoxide was determined using a JEOL model C-60H spectrometer with tetramethylsilane(TMS) as the reference, the concentration used being 20 wt%.

1.2. Ligand. Commercially-available diethylenetriamine was further purified by vacuum distillation.

1.3. Synthesis of the Isomers. The complex was prepared as mixtures of isomers by the following four methods.

Method A: Cooled diethylenetriamine (7.7 g) was dissolved in 30 m*l* of cold water, and to this solution 14 g of $K_3[Co(CO_3)_3] \cdot 3H_2O$[15] was added in small portions with vigorous stirring. The mixture was kept at 0—3°C during the reaction for about one hour. One gram of active charcoal was then added and stirring was continued for 5 hr. After the solution had been kept at 0°C overnight, 100 m*l* of ice water and then 25 m*l* of concentrated hydrobromic acid were slowly added under cooling (5—10°C). After the evolution of carbon dioxide, the active charcoal was filtered off and the filtrate was evaporated to half the volume. The crystallized yellowish needles were filtered, recrystallized from water, washed with aqueous ethanol (1:1), and dried in air. The yield of the complex bromide, which was named the isomer A, was about 1 g. The above reaction mixture contained three isomers, and the formation ratio was found to be: *s-facial*: *u-facial*: *mer*=16:25:59 by separation on an SE-Sephadex column and by subsequent spectrophotometric determination (*cf.* 1.4).

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[1] A part of the present investigation was published as a preliminary report: F. R. Keene, G. H. Searle, Y. Yoshikawa, A. Imai, and K. Yamasaki, *Chem. Commun.*, **1970**, 784.

[2] F. G. Mann, *J. Chem. Soc.*, **1934**, 466.

[3] P. Job and J. Brigando, *Compt. rend.*, **210**, 438 (1940); **236**, 708 (1953); J. Brigando, *Bull. Soc. Chim. Fr.*, **1957**, 211, 221.

[4] H. H. Schmidtke, *Z. physik. Chem.*, **38**, 170 (1963).

[5] F. Basolo, J. W. Palmer, and R. G. Pearson, *J. Amer. Chem. Soc.*, **82**, 1073 (1960).

[6] W. C. Fernelius and B. E. Bryant, *ibid.*, **75**, 1735 (1953).

[7] P. H. Crayton and J. A. Mattern, *J. Inorg. Nucl. Chem.*, **13**, 248 (1960).

[8] A. M. Sargeson, "Chelating Agents and Metal Chelates," Academic Press, New York (1964), p. 183.

[9] G. G. Schlessinger, "Werner Centennial," American Chemical Society (1967), p. 565.

[10] A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **6**, 787 (1967).

[11] Y. Yoshikawa and K. Yamasaki, *Inorg. Nucl. Chem. Lett.*, **4**, 697 (1968).

[12] A. Werner, *Ber.*, **45**, 127 (1912).

[13] A. J. McCaffery and S. F. Mason, *Mol. Phys.*, **6**, 359 (1963).

[14] J. H. Dunlop, R. D. Gillard, and G. Wilkinson, *J. Chem. Soc.*, **1964**, 3160.

[15] M. Mori, M. Shibata, E. Kyuno, and T. Adachi, This Bulletin, **29**, 883 (1956); M. Shibata, M. Mori, and E. Kyuno, *Inorg. Chem.*, **3**, 1573 (1964).

Method B: To 50 g of [CoBr(NH)$_3$)$_5$]Br$_2$ suspended in 400 m*l* of water, 2 g of active charcoal was added, and then 30 g of diethylenetriamine was slowly added in about one hour. Ammonia was evolved, and then the stirring was continued for 24 more hours at 25°C. The charcoal was then filtered off, and the filtrate was evaporated to half its volume under reduced pressure. Large amounts of ethanol and diethyl ether were then added until the precipitation was complete. The yellowish-brown powder thus obtained was filtered and washed several times with 1-butanol and once with diethyl ether, and then dried in air. The yield was 65.5 g. This product is a mixture of three isomers with the formation ratio of *s-facial: u-facial: mer*=7:30:63, which was determined by separation on an SE-Sephadex column as has been described above.

Method C: A mixture of isomers was also obtained by adding diethylenetriamine to a cobalt chloride solution in the presence of active charcoal and by then oxidizing the reaction mixture with air or hydrogen peroxide. This method gave almost the same results as the method B.

Method D: To 2 m*l* of diethylenetriamine, 0.8 g of finely ground *mer*-[CoCl$_3$(dien)][7] was added. The mixture was well triturated for about 20 min in an ice-bath, and then the the excess diethylenetriamine was thoroughly washed away with 1-butanol. The remaining solid was dissolved in a small amount of water, and the isomers were separated by column chromatography as has been described in 1.4. The product obtained contained only the *u-facial* and *mer* isomers in the ratio of 8:92. This preparative method is not an equilibrium one, but was used for confirming the configurational assignment of the *mer* (the isomer C).

1.4. *Separation of the Isomers.* Since the separation of three isomers by the conventional fractional crystallization technique was unsatisfactory and laborious, a chromatographic method using ion-exchange Sephadex[16] and cellulose was developed. The SE-Sephadex used was a product of Pharmacia, Sweden, with a particle size of 40—120 μ and an ion-exchange capacity of 2.3±0.3 meq/g. A mixture of the isomers obtained by one of the above methods, A, B, C, or D, was poured on an SE-Sephadex column (diameter, 3.0 cm; length, 120 cm) and eluted with a 0.15 M sodium $(+)_{589}$-tartrate solution at the rate of 1.2—1.4 m*l* per minute. Three completely-separated bands were thus obtained. The fastest moving complex was named A; the middle one, B, and the slowest one, C. The isomer A is the same as the one which is least soluble among the products obtained by the method A. Three isomers, A, B, and C, were found by experiments to be described in the later sections, to be *s-facial*, *u-facial*, and *mer* isomers respectively. Eluted fractions of the isomer B were optically active, indicating a partial resolution. Consequently, the isomer B was identified as the *u-facial* isomer. An example of the separation experiment is shown in Fig. 2.

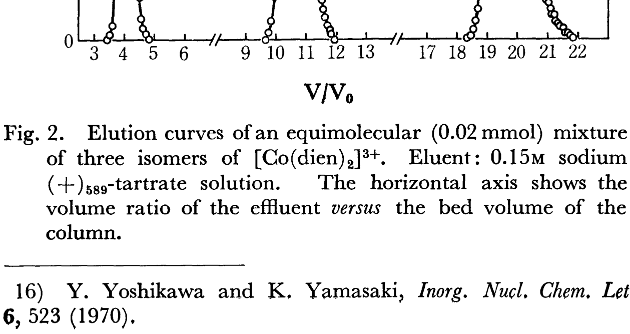

Fig. 2. Elution curves of an equimolecular (0.02 mmol) mixture of three isomers of [Co(dien)$_2$]$^{3+}$. Eluent: 0.15M sodium $(+)_{589}$-tartrate solution. The horizontal axis shows the volume ratio of the effluent *versus* the bed volume of the column.

The isomers could also be separated on a P-cellulose column (100 cm long), using 1-butanol saturated with water as the solvent, and a mixture of 1-butanol, concentrated hydrochloric acid, and water in a ratio of 200:15:15 as the eluent. First, the *mer*, then *s-facial*, and lastly *u-facial* isomers were eluted. Each isomer was back-extracted into the water phase, which was then evaporated to dryness. The chlorides thus obtained were recrystallized from water, washed quickly with an equal mixture of water and ethanol, and then dried in air.

The bromides of the *mer* and *u-facial* isomers were prepared by passing the respective chlorides through an ion-exchange resion column of the bromide form. The *s-facial* bromide was obtained as the least soluble isomer by the method A. The *mer* iodide was obtained by converting the chloride on an ion-exchange resin column of the iodide form. The *u-facial* and *s-facial* iodides were precipitated when potassium iodide was added to solutions of the *u-facial* and *s-facial* chlorides respectively.

1.5. *Resolution of the* u-Facial *and* Mer *Isomers.* The chromatographic method using SE-Sephadex described in 1.4 was also applied, with minor modifications, to the complete resolution of the *u-facial* and *mer* isomers. When eluted by a sodium $(+)_{589}$-tartrate solution, the adsorbed *u-facial* isomer was not clearly separated into two bands, but the initial and last several fractions indicated an almost complete resolution. The use of a 0.3 M sodium antimony $(+)_{589}$-tartrate solution instead of a sodium $(+)_{589}$-tartrate solution caused the two bands corresponding to $(+)_{589}$ and $(-)_{589}$ antipodes to be completely separated in the column. The fast-moving band corresponds to the $(+)_{589}$-antipode with the CD value of $\Delta\varepsilon_{502}=+0.98$ and the molar rotation of $[M]_{589}=+211°$ (*cf.* Fig. 3). The optically-active complexes, both $(+)_{589}$ and $(-)_{589}$, have the same chemical composition, [Co(dien)$_2$]·Cl$_3$·H$_2$O, while the racemic complex has two moles of water of crystallization.

The resolution of the *mer* isomer was first carried out by Searle and Keene[17] by the conventional fractional crystallization of the diastereoisomers. The chromatographic method used in the resolution of the *u-facial* isomer has been successfully applied by us to the resolution of the *mer* isomer as well. The *mer* isomer adsorbed on a column of SE-Sephadex was eluted by a 0.3 M sodium antimony $(+)_{589}$-tartrate solution. First $(+)_{589}$ and then $(-)_{589}$ antipodes were eluted with complete separation. The effluents thus obtained were diluted five times, and then they were again adsorbed on columns of SE-Sephadex. After the columns had been washed with 0.01 N hydrochloric acid, each antipode was eluted with 1 N NaCl containing 0.01 N HCl. To the effluents, potassium hexacyanocobaltate(III) was added. The sparingly soluble yellowish crystals thus obtained were suspended in 0.01 N HCl with an ion-exchange resin (Dowex 1X8) in the chloride form. After the solution had been stirred for 2 hours, the resin was filtered off. The filtrate which contained the optically-active chloride was again

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

17) F. R. Keene, G. H. Searle, and S. F. Mason, *Chem. Commun.*, **1970**, 893.

passed through a column of Dowex (chloride form) to ensure its conversion into the chloride, and then it was evaporated to dryness. The resulting chloride was dissolved in water and precipitated by adding ethanol. The rotation observed for $(+)_{589}$-*mer*-[Co(dien)$_2$]Cl$_3$ has its maximum at 484 mμ with the value of $[M]_{589}=-658°$ (*cf* Fig. 4). The half-time of the racemization of the aqueous solution is about 4 weeks at room temperature.

Results and Discussion

2.1. Chemical Compositions. The three isomers have the chemical compositions shown in Table 1; they have been characterized by a study of their infrared, electronic, and PMR spectra.

TABLE 1. CHEMICAL COMPOSITION OF THE ISOMERS

Complex	Elemental analyses (Calcd value)			
	Co	Halogen	N	H_2O
s-facial [Co(dien)$_2$]Cl$_3$·H$_2$O	15.05 (15.12)	27.08 (27.30)	—	4.58% (4.62)
[Co(dien)$_2$]Br$_3$	11.58 (11.67)	47.41 (47.47)	16.70 (16.64)	
[Co(dien)$_2$]I$_3$	9.29 (9.12)	58.93 (58.94)	— —	
u-facial [Co(dien)$_2$]Cl$_3$·2H$_2$O$^{a)}$	14.38 (14.46)	25.88 (26.09)	—	8.78 (8.84)
[Co(dien)$_2$]Br$_3$·H$_2$O	11.25 (11.27)	45.87 (45.87)	16.29 (16.07)	3.53 (3.44)
[Co(dien)$_2$]I$_3$·H$_2$O	8.91 (8.88)	57.27 (57.33)	— —	2.60 (2.71)
mer [Co(dien)$_2$]Cl$_3$·2½H$_2$O	14.03 (14.14)	25.13 (25.53)	— —	10.81 (10.81)
[Co(dien)$_2$]Br$_3$·2H$_2$O	10.74 (10.89)	44.07 (44.31)	15.65 (15.53)	7.10 (6.67)
[Co(dien)$_2$]I$_3$·½H$_2$O	8.94 (9.00)	58.25 (58.39)	— —	1.17 (1.38)

a) Optically active antipodes, both $(+)_{589}$ and $(-)_{589}$, have one mol of water of crystallization.

The isomer B has been proved to have the *u-facial* structure by its resolution into optical antipodes. The *mer* isomer is also resolvable, but its optical activity is less stable than that of the *u-facial* isomer.[17] The *s-facial* isomer cannot be resolved because it has a center of symmetry. The X-ray crystal analysis of *s-facial*-[Co(dien)$_2$]Br$_3$ has recently been carried out by Saito *et al.* This complex cation has a center of symmetry with an approximate C_{2h} symmetry.[18]

The distinction between *mer* and *s-facial* isomers was made by studying the PMR spectrum. The preparative method D also afforded additional evidence for the meridional structure of the isomer C.

2.2. Circular Dichroism Spectrum. The structure of the two complex ions, [Co(dien)$_2$]$^{3+}$ and [Co(penten)]$^{3+}$, are closely related; they are different only in that a fifth chelate ring joining the two secondary nitrogen atoms is present in the latter (*cf.* Fig. 1). Therefore, the absolute configuration of [Co(penten)]$^{3+}$ may give a clue to the elucidation of that of the *u-facial*-[Co(dien)$_2$]$^{3+}$. The X-ray crystal analysis of $(+)_{589}$-[Co(en)$_3$]$^{3+}$ [19] and $(+)_{589}$-[Co(penten)]$^{3+}$ [20] showed that both ions have the same Λ configuration in terms of the IUPAC nomenclature.[21] The absolute configuration of the latter ion has also been assigned on the basis of the stereospecificity of the methylated penten.[22]

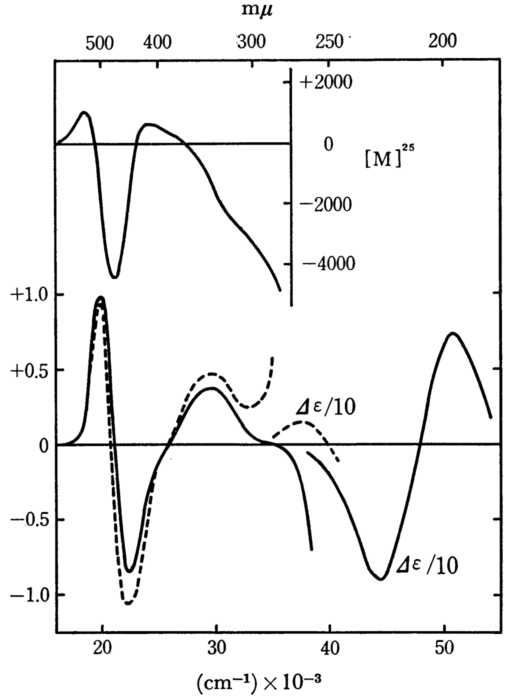

Fig. 3. Optical rotatory dispersion (upper curve) and circular dichroism (lower curve) spectra of $(+)_{589}$-*u-facial* [Co(dien)$_2$]Cl$_3$; ——in water and······in 0.2M Na$_2$SeO$_3$.

The relationship between the absolute configuration and the CD spectrum of $(+)_{589}$-[Co(en)$_3$]$^{3+}$ has been well established. This complex has a major positive band and a minor negative band at a lower and a higher frequency in the region of the octahedral ${}^1A_{1g}\rightarrow T^1_{1g}$ absorption, the area of these CD bands being diminished and enhanced respectively by the addition of selenite or phosphate ions.[23,24] The same relationship holds also for $(+)_{589}$-[Co(penten)]$^{3+}$.[22] The ORD and CD curves of $(+)_{589}$-*u-facial*-[Co(dien)$_2$]$^{3+}$ are shown in Fig. 3. The CD spectrum shows a lower-energy positive ($\Delta\varepsilon=+0.98$, 19900 cm^{-1}) and a higher-energy negative ($\Delta\varepsilon=-0.84$, 22500 cm^{-1}) component in the region of the first ligand-field band. Further, another positive component ($\Delta\varepsilon=+0.37$, 29900 cm^{-1}) exists in the region of the second band, and intense negative and positive components ($\Delta\varepsilon=-9.0$, 44400 cm^{-1} and $\Delta\varepsilon=+7.4$, 50700 cm^{-1}) in the region of the charge-transfer band. Since the sign and magnitude of the

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[18] Y. Saito, private communication.

[19] Y. Saito, K. Nakatsu, M. Shiro, and H. Kuroya, *Acta Crystallogr.*, **8**, 729 (1955); This Bulletin, **30**, 158, 795 (1957).

[20] A. Muto, F. Marumo, and Y. Saito, *Inorg. Nucl. Chem. Lett.*, **5**, 85 (1969); *Acta Crystallogr.*, **B26**, 226 (1970).

[21] *IUPAC Information Bull.*, No. 33, 68 (1968); *Inorg. Chem.*, **7**, 1 (1970).

[22] Y. Yoshikawa, E. Fujii, and K. Yamasaki, *Proc. Japan Acad.*, **43**, 495 (1967), and the references cited therein; J. R. Golgogy and C. J. Hawkins, *Chem. Commun.*, **1966**, 873.

[23] H. L. Smith and B. E. Douglas, *J. Amer. Chem. Soc.*, **86**, 3885 (1964); *Inorg. Chem.*, **5**, 784 (1966).

[24] S. F. Mason and B. J. Norman, *Proc. Chem. Soc.*, **1964**, 339; *J. Chem. Soc.*, *A*, **1966**, 307.

CD bands of $(+)_{589}$-*u-facial*-[Co(dien)$_2$]$^{3+}$ are similar to those of $(+)_{589}$-[Co(en)$_3$]$^{3+}$ and $(+)_{589}$-[Co(penten)]$^{3+}$, it may be concluded that these three complexes have the same absolute configuration, Λ, those of the dien and penten complexes being shown in Fig. 1.

Further, from a consideration of the sign of the CD band in the charge-transfer region,[25] each five-membered chelate ring can be presumed to have the conformation shown in Fig. 1. The X-ray determination of the absolute configuration of the $(+)_{589}$-*u-facial*-[Co(dien)$_2$]$^{3+}$ is now under way by Prof. Y. Saito, University of Tokyo. Both the ring-pairing method[26] and the octant rule[27] support the absolute configuration proposed here.

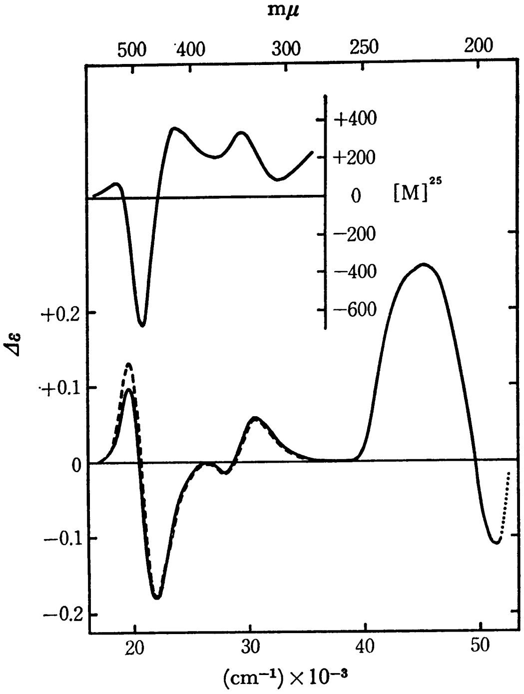

Fig. 4. Optical rotatory dispersion (upper curve) and circular dichroism (lower curve) spectra of $(+)_{589}$-*mer*-[Co(dien)$_2$]Cl$_3$; ——in water and ······in 0.2 M Na$_2$SO$_4$.

In Fig. 4 the ORD and CD curves of the $(+)_{589}$-*mer*-[Co(dien)$_2$]Cl$_3$ are shown. The CD spectrum has peaks split into two in the regions of the $^1A_{1g}\rightarrow{}^1T_{1g}$ ($\Delta\varepsilon=+0.096$, 19500 cm^{-1}; $\Delta\varepsilon=-0.181$, 21900 cm^{-1}) and $^1A_{1g}\rightarrow{}^1T_{2g}$ ($\Delta\varepsilon=-0.014$, 27800 cm^{-1}; $\Delta\varepsilon=+0.057$, 30700 cm^{-1}) transitions; these are much less intense than those of the $(+)_{589}$-*u-facial* isomer. In the charge-transfer region, a CD peak with a weak intensity is observed. The $(-)_{589}$-antipode shows an identical CD spectrum with the opposite sign. In 0.2 M sodium sulfate, the intensity of the lower-energy band in the first absorption region is enhanced, while the other peaks are affected very little. Sodium sulfate is used because sodium selenite commonly used accelerates the racemization because of the increase in the pH. The optically-active *mer* isomer is stable only in the pH region lower than 6.

In the structure of the *mer* isomer shown in Fig. 1, both the skew chelate pairs, 1,3 and 2,4 have the Λ (δ, λ) configuration, while the pairs, 2,3 and 1,4 have the $\Delta(\delta, \delta)$ and $\Delta(\lambda, \lambda)$ configurations respectively. This isomer, therfore, has, as a whole, an equal number of Δ and Λ configurations, and δ and λ conformations. Thus, the dissymmetric effects seem to be cancelled out. Nevertheless, CD peaks, though very weak, are observed; they may be due to the integration of the three different configuraions and conformations mentioned above.

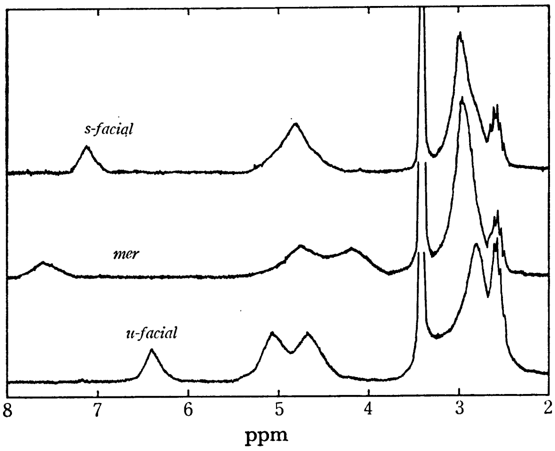

Fig. 5. PMR spectra of *s-facial* (curve 1,) *mer*(curve 2) and *u-facial* (curve 3) isomers of [Co (dien)$_2$]I$_3$ in deuterated DMSO.

2.3. *PMR Spectrum.* Figure 5 shows the PMR spectra of the three isomers taken in deuterated dimethylsulfoxide. The isomer A shows broad signals at δ 4.80 and 7.12 (intensity ratio 4: 1); the isomer C at δ 4.18, 4.75, and 7.60 (intensity ratio 2: 2: 1), and the isomer B, at δ 4.68, 5.08, and 6.40 (intensity ratio 2: 2: 1). From the intensities, the siganls at δ 4.0—5.5 are assigned to the protons in NH$_2$ groups, and those in the lower field, to the protons in NH groups, both of which are broadened by the quadrupole relaxation of the ^{14}N nucleus.[28]

The signal at δ 3.4 is due to water remaining in the solution, and that at δ 2.5—2.6, to residual CH$_3$ groups in the deuterated solvent. Further, the signals of methylene groups appear at δ 2.7—3.0. As is clear from the structures shown in Fig. 1 the NH$_2$ signals for the *mer* and *u-facial* isomers should be split into two, while only one signal can be expected for the *s-facial* isomer.

In the *s-facial* isomer, the NH$_2$ groups are equivalent, while the other two isomers have unequivalent sets of two NH$_2$ groups. The observed results agree with the expectation, and so the isomer A is identified as *s-facial.* The signal due to two equivalent NH groups of the *u-facial* isomer should be in the highest field because the two central nitrogen atoms may be displaced from the

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[25] K. Ogino, K. Murano, and J. Fujita, *Inorg. Nucl. Chem. Lett.*, **4**, 351 (1968).

[26] J. I. Legg and B. E. Douglas, *J. Amer. Chem. Soc.*, **88**, 2967 (1966).

[27] C. J. Hawkins and E. Larsen, *Acta Chem. Scand.*, **19**, 185 (1965).

[28] J. A. Pople, *Mol. Phys.*, **1**, 168 (1958).

octahedral positions by large non-bonded interactions around them, while that of the *mer* isomer should be in the lowest fields (*cf.* 2.4). On the basis of these results, the isomer A, B, and C are identified as *s-facial*, *u-facial*, and *mer* respectively. Yoneda *et al.*[29] reported the PMR spectrum of $[Co(dien)_2]Cl_3$ in trifluoroacetic acid without referring to the isomerism. Judging from the reported spectrum, their sample seems to be the *mer* isomer.

2.4. Electronic Absorption Spectrum. The absorption spectra of the three isomers in the region 18000—52500 cm^{-1} are shown in Table 2 and Fig. 6. By stereochemistry the *mer* isomer is more distorted from a regular octahedron than the other two. Consequently, it may reasonably be concluded that the distortion of the ligand molecule makes the Co–N(secondary) bond length shorter than the Co–N(primary) bond length, and that two terminal nitrogen(primary) atoms are considerably displaced from the apices of a regular octahedron. This expected difference in bond lengths has been found by X-rays for several complexes, as shown in Table 3.

TABLE 2. ABSORPTION SPECTRA

Complex	First band $^1A_{1g} \rightarrow {}^1T_{1g}$	Second band $^1A_{1g} \rightarrow {}^1T_{2g}$	CT band N(σ) $\rightarrow e_g(\sigma^*)$	CT band (halide ion)
s-facial $[Co(dien)_2]Cl_3$	21800 (66.5)	30000 (61.0)	47400cm^{-1} (21700)	
u-facial	21500 (93.0)	29700 (88.5)	46300 (22600)	
mer	21600 (146)	29300 (107)	44400 (21200)	
s-facial $[Co(dien)_2]Br_3$	21800 (66.5)	30000 (60.5)	~45500sh (21100)	51000 (50300)
u-facial	21500 (93.4)	29800 (89.2)	~45500sh (23500)	51000 (47400)
mer	21600 (141)	29300 (106)	~44400sh (22900)	51300 (45500)
s-facial $[Co(dien)_2]I_3$	21800 (69.6)	31000sh (101)	44600[a] (58800)	51300 (58900)
u-facial	21500 (94.5)	30200 (121)	44600[a] (61900)	51300 (54100)
mer	21600 (140)	29900 (136)	44400[a] (64300)	51500 (50000)

Figures in the parentheses are molar extinction coefficients.
sh: shoulder, CT: charge transfer.
a) The band due to iodide ion is superposed on this CT band.

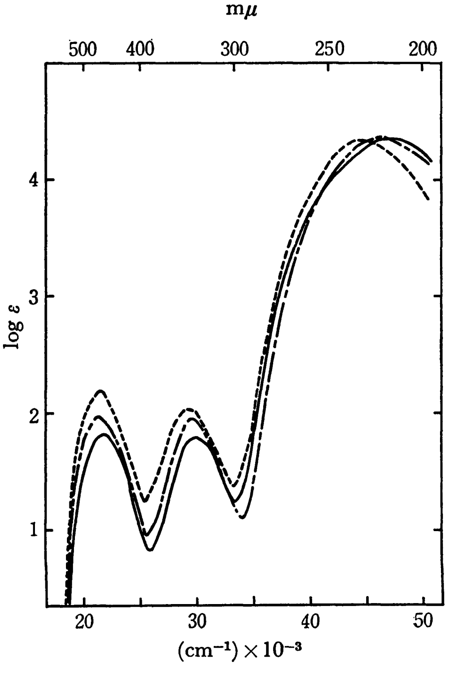

Fig. 6. Absorption spectra of three isomers of $[Co(dien)_2]Cl_3$ in water; —— *s-facial*, ······ *mer* and —·—*u-facial*.

TABLE 3

Complex	M-NH	M-NH$_2$	Ref.
mer-$[Co(NO_2)gly(dien)]Cl \cdot H_2O$	1.91Å	1.94Å	30
mer-$[CoCl(gly)(dien)]ClO_4$	1.94	1.99	30
mer-$[Ni(dien)_2]Cl_2 \cdot H_2O$	2.05	2.16	31

If the conformational structure (δ,λ) of each chelate ring is not taken into consideration, the *s-facial* isomer can be said to have a center of symmetry,[18] while the other two have none, and the structures of the latter two may deviate considerably from an octahedron. This expectation agrees with the intensity of the *d-d* absorption bands shown in Table 2. On the other hand, the first ligand field bands, which are observed at 21800, 21600, and 21500 cm^{-1} for *s-facial*, *mer*, and *u-facial* isomers respectively, reveal that the ligand field is highest for the *s-facial* isomer and lowest for the *u-facial* isomer. In spite of the strained structure, the *mer* isomer has a higher ligand field than the *u-facial* isomer. Presumably it contributes to this result that the Co–N(secondary) bond in the *mer* isomer is appreciably stronger than the others. The above result is consistent with the PMR results.

By comparing the absorption bands reported by Brigando[3] and Schmidtke[4] with those of the present investigation, we find that the sample used by Brigando seems to be a mixture of the *mer* and *u-facial* isomers, while that of the latter investigator is the *mer* isomer.

2.5. Infrared Spectra. Recently Schmidtke and Garthoff[32] studied in detail the infrared spectra of the geometric isomers of mono(diethylenetriamine)

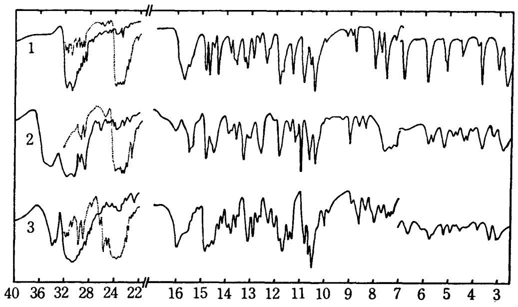

Fig. 7. Infrared spectra of *s-facial* (curve 1), *mer* (curve 2), and *u-facial* (curve 3) isomers of $[Co(dien)_2]Br_3$. ······ deuterated complexes.

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[29] H. Yoneda and Y. Morimoto, This Bulletin, **39**, 2180 (1966).

[30] H. Kuroya, private communication.

[31] P. Paoletti, S. Biagini, and M. Cannas, *Chem. Commun.*, **1969**, 513.

[32] H. H. Schmidtke and D. Garthoff, *Inorg. Chim. Acta*, **2**, 357 (1968).

complexes of Rh(III), Cr(III), and Co(III), and concluded that the *facial* and *meridional* isomers can be distinguished by different spectral features. Buckingham and Jones[33] have also studied the infrared spectra of isomers of diacido(triethylenetetramine)cobalt(III) complexes. On the basis of these results, and also of those of ethylenediamine complexes, the infrared spectra of $[Co(dien)_2]Br_3$ are assigned. The spectra in the region 4000—300 cm^{-1} are shown in Fig. 7.

In all three isomers the NH stretching vibrations observed at 3200—3000 cm^{-1} shift to 2400—2250 cm^{-1} on deuteration, with the ratio of $\nu_{NH}/\nu_{ND}=1.33$—1.34. The frequency of these vibrations is highest for the *u-facial*, medium for the *mer*, and lowest for the *s-facial* isomers. For the *mer* isomer, a medium strong band appears at 2848 cm^{-1} and this shifts to 2128 cm^{-1} on deuteration ($\nu_{NH}/\nu_{ND}=1.35$), while the other two show only very weak bands in this region. Therefore, this band may be characteristic of the *mer* isomer, and it can tentatively be assigned to the NH stretching vibration of the secondary amine.

The absorption bands at 1610—1550 cm^{-1} shift on deuteration to 1220—1150 cm^{-1} with the ratio of $\nu_{NH}/\nu_{ND}=1.32$—1.36; therefore, they are identified as antisymmetric NH_2 bending vibrations. The *mer* isomer showed a larger splitting in the same region; it may be due to the two unequivalent NH_2 groups. In the region lower than 600 cm^{-1}, the bands due to ring deformation and those related to the Co–N bonds coupled with them are observed. Generally the *s-facial* isomer shows fewer and sharper bands than the other two, as is to be expected from its higher symmetrical structure.

A near-infrared band of HDO was used to study the kinetics of proton exchange[34] in these three isomers; it was found that the NH group exchanged protons faster than the NH_2 group of the ligand and that, further, the rate of the exchange of the NH group of the *mer* isomer is largest among the three isomers.[35] This fact is consistent with the position of the NH signal of the *mer* isomer in the lowest magnetic field (*cf.* 2.3).

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33) D. A. Buckingham and D. Jones, *Inorg. Chem.*, **4**, 1378 (1965).

34) H. Yamatera and M. Fujita, This Bulletin, **42**, 3043 (1969).

35) H. Yamatera, private communication.