Studies of 4-Diethylenetriaminemonoacetatocobalt(III) Complexes. I. The Preparation and Identification of 4-Diethylenetriaminemonoacetatocobalt(III) Complexes with Ethylenediamine, Oxalate Ion, or Acetylacetonate Ion as the Additional Ligand

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The *fac(N)*- and *mer(N)*-isomers of 4-diethylenetriaminemonoacetatocobalt(III) complexes with ethylenediamine, the oxalate ion, or the acetylacetonate ion as the additional ligand have been obtained by means of reactions between chloro(4-diethylenetriaminemonoacetato)aquocobalt(III) chloride and the bidentates under different conditions. The geometrical configuration of each isomer has been identified by means of the PMR spectra and the electronic absorption spectra. The methine hydrogen in the acetylacetonato complexes has been replaced with bromine, and the resulting complexes have also been characterized.

4-Diethylenetriaminemonoacetate $(NH_2\text{–}CH_2\text{–}CH_2\text{–}\overset{\displaystyle CH_2\text{–}COO^-}{\overset{|}{N}}\text{–}CH_2\text{–}CH_2\text{–}NH_2$, abbreviated as *i*-DTMA* in this article) is a tetradentate of the $A{<}\begin{array}{l}B\\C\\B\end{array}$ type. It is capable of coordinating to the cobalt(III) ion in two different modes, as is shown in Fig. 1. As a result, a di(unidentate)-(*i*-DTMA)-Co(III) aggregate and a (*s*-bidentate)-(*i*-DTMA)-Co(III) aggregate may exist in two stereoisomers, and a (*uns*-bidentate)-(*i*-DTMA)-Co(III) aggregate, in four. Schneider and Collman1) first dealt with the cobalt(III) complexes with the tetradentate. They prepared one isomer in the dinitro, the dichloro, or the carbonato complex, and two isomers in the glycinato complex. They tentatively identified the coordination mode as *fac*(*N*) in all of their complexes; their assignment is considered to be correct. No cobalt(III) complex having the tetradentate with the *mer*(*N*)-mode has been isolated so far.

In the course of our previous studies of cobalt(III) complexes containing triethylenetetramine (trien),2) ethylenediamine-*N*,*N'*-diacetate (EDDA),3) and 1-diethylenetriaminemonoacetate (DTMA),4) ** we observed that the coordination mode of the ligands depends largely upon the reaction temperature of the preparations and also, to some extent, upon the kind of ligand occupying the residual coordination sites. Therefore, it was supposed that the *mer*(*N*)-mode of the tetradentate, which was probably the more unstable and difficult mode, would occur as a result of a reaction at high temperatures. Thus, two isomers were obtained in the ethylenediamine, the oxalato, and the acetylacetonato complexes. This report will deal with their preparation and characterization.

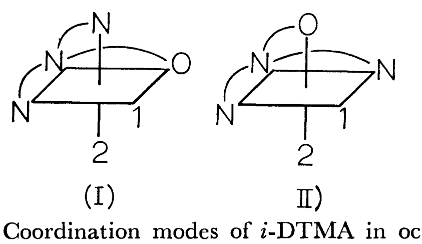

Fig. 1. Coordination modes of *i*-DTMA in octahedral complexes.
(I) *fac*(*N*)-configuration, (II) *mer*(*N*)-configuration.

Experimental

Materials, Analysis, Apparatus, and Measurements. All the chemicals were of a reagent grade and were used without further purification. The carbon, hydrogen, and nitrogen in the synthesized complexes were analysed by the Analyses Center of the Institute for Chemical Research, Kyoto University. The visible and ultraviolet absorption spectra were measured in aqueous solutions with a Hitachi EPS-3 Recording Spectrophotometer. The PMR spectra were recorded with a Japan Electron Optics JNM-100 Spectrometer (100 MHz), using deuterium oxide as the solvent and *tert*-butyl alcohol as the internal reference. The temperature of the probe was maintained at 22±1 °C.

Preparation. *(1)* fac(N)-*Chloro(4-diethylenetriaminemonoacetato)aquocobalt(III) Chloride Monohydrate*, fac(N)-[*Co(*i-*DTMA)Cl(H_2O)*]*Cl*·H_2O: Dinitro(4-diethylenetriaminemonoacetato)cobalt(III) monohydrate, [Co(*i*-DTMA)-$(NO_2)_2$]·H_2O, was prepared by the method of Schneider and Collman.1) One gram of the dinitro complex was dissolved in 10 ml of hydrochloric acid (6 M) by heating, and the resulting solution was evaporated to dryness with the aid of an air stream blown onto the surface. During the dissolution, nitric oxides were evolved, and finally a greenish blue residue was obtained. (This is probably the dichloro complex.) A small amount (~3 ml) of water was then mixed with the residue, which dissolved at once, forming a violet solution. A bright violet precipitate soon appeared. The precipitate was transferred onto a filter with a methanol (80%)–water mixture and then washed with methanol and ether. Yield, 0.8 g. By treating the filtrates of the above procedure in the same way, an additional product was obtained. The total yield was 0.95 g.

Found: C, 21.80; H, 5.86; N, 12.58%. Calcd for [Co(*i*-DTMA)Cl(H_2O)]Cl·H_2O = $CoC_6H_{18}O_4N_3Cl_2$(326.07): C, 22.10; H, 5.56; N, 12.89%.

(2) mer(N)-*Chloro(4-diethylenetriaminemonoacetato)aquocobalt(III) Perchlorate*, mer(N)-[*Co(*i-*DTMA)Cl(H_2O)*]*ClO_4*:

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* This abbreviation follows that of Schneider and Collman.1)

** The following abbreviations are used in this article besides these ligands: en, ethylenediamine; acac, acetylacetonate; Bracac, 3-bromo-2,4-pentanedionate (bromoacetylacetonate); ox, oxalate; gly, glycinate.

Into 5 ml of 2 M $HClO_4$ 0.5 g of the *fac*(*N*)-chloroaquo complex (1) was added, after which the mixture was heated on a boiling water bath. The starting complex dissolved at once; dark violet crystals then appeared. After heating for 15 min, the crystals were collected and washed with a small amount of cold water, methanol, and ether. Yield, 0.5 g. By the evapoartion of the filtrate, an additional product was obtained. The total yield was 0.55 g.

Found: C, 19.20; H, 4.53; N, 11.18%. Calcd for [Co(*i*-DTMA)Cl(H_2O)]ClO_4 = $CoC_6H_{16}O_7N_3Cl_2$ (372.05): C, 19.37; H, 4.33; N, 11.29%.

(3) fac (N)-*4-Diethylenetriaminemonoacetato(ethylenediamine)-cobalt(III) Perchlorate,* fac(N)-*[Co(*i-*DTMA)(en)](ClO$_4$)$_2$*: After a solution which contained 0.6 g of the *fac*(*N*)-chloroaquo complex in 10 ml of water had been heated for 15 min on a boiling-water bath, 0.6 ml of aqueous ethylenediamine (20%) and 0.1 g of active charcoal were added to the solution, in this order. Upon the addition of the charcoal, the color rapidly changed to a brownish orange. The mixture was then heated for 5 min, the charcoal was removed by filtration, and 1 ml of 6 M $HClO_4$ was added; a large amount of deep orange precipitate appeared upon cooling. After the product had been allowed to stand for 1 hr in a refrigerator, the precipitate was separated and recrystallized from 25 ml of warm (~60 °C) water with the addition of a few drops of 6 M $HClO_4$. Yield, 0.6 g.

Found: C, 19.97; H, 4.77; N, 14.67%. Calcd for [Co(*i*-DTMA)(en)](ClO_4)$_2$ = $CoC_8H_{22}O_{10}N_5Cl_2$ (476.13): C, 20.10; H, 4.64; N, 14.65%.

(4) mer (N)-*4-Diethylenetriaminemonoacetato(ethylenediamine)-cobalt(III) Perchlorate,* mer(N)-*[Co(*i-*DTMA)(en)](ClO$_4$)$_2$*: The filtrate obtained in the preparation of the *fac*(*N*)-isomer was concentrated to ~2 ml and then cooled; a pale yellowish orange precipitate thus appeared. It was recrystallized from 2 ml of warm water with the addition of a few drops of 6 M $HClO_4$. Yield, 0.1 g.

Found: C, 19.84; H, 4.70; N, 14.45%. Calcd for [Co(*i*-DTMA)(en)](ClO_4)$_2$ = $CoC_8H_{22}O_{10}N_5Cl_2$ (476.13): C, 20.10; H, 4.64; N, 14.65%.

(5) fac (N)-*Oxalato(4-diethylenetriaminemonoacetato)cobalt(III),* fac(N)-*[Co(*i-*DTMA)(ox)]*: A mixture of 0.3 g of the *fac*(*N*)-chloroaquo complex (1) and 0.13 g of oxalic acid dihydrate in 5 ml of water was heated at ~65 °C for 30 min with stirring. Reddish violet crystals came out during the reaction. After the product had been cooled in an ice-water bath for 3 hr, the crystals were collected and recrystallized from 30 ml of hot (~80 °C) water. Yield, 0.2 g.

Found: C, 30.93; H, 4.54; N, 13.81%. Calcd for [Co(*i*-DTMA)(ox)]=$CoC_8H_{14}O_6N_3$(307.15): C, 31.28; H, 4.59; N, 13.68%.

(6) mer(N)-*Oxalato(4-diethylenetriaminemonoacetato)cobalt(III) Dihydrate,* mer(N)-*[Co(*i-*DTMA)(ox)]·2H$_2$O*: A solution of 0.3 g of the *fac*(*N*)-chloroaquo complex (1) in 5 ml of water was heated in a boiling-water bath for 15 min. Another solution, which contained 0.13 g of sodium oxalate in 5 ml of water, was also heated to 100 °C. Then the solutions were combined, and the mixture was kept at 100 °C for 10 min; a deep red solution was thus obtained. After the solution had been cooled in an ice-water bath for 1 hr, the red precipitate formed was collected on a filter and then fractionally extracted with 10 ml portions of warm (~60 °C) water four times. In the first extract (red-colored), an orange-red precipitate amounting 0.15 g was deposited by adequate cooling. The precipitate from the second extract contained the red-violet *fac*(*N*)-isomer to some extent. The deposits in the third and the fourth extracts consisted entirely of the *fac*(*N*)-isomer. The product from the first extract was recrystallized with 5 ml of warm water. Yield, 0.1 g.

Found: C, 27.88; H, 5.41; N, 12.35%. Calcd for [Co(*i*-DTMA)(ox)]·$2H_2O$=$CoC_8H_{18}O_8N_3$(343.18): C, 28.00; H, 5.29; N, 12.24%.

(7) fac (N)-*Acetylacetonato(4-diethylenetriaminemonoacetato)-cobalt(III) Perchlorate,* fac (N)-*[Co(*i-*DTMA)(acac)]ClO$_4$*: A solution of the *fac*(*N*)-chloroaquo complex (0.5 g) in 10 ml of water was heated in a boiling-water bath for 15 min. Another solution, which contained acetylacetone (0.2 g) and sodium hydroxide (0.08 g) in 10 ml of water, was also heated to 100 °C and was then mixed with the former by stirring. The color of the mixture soon changed from blue to dark red. After the addition of 1 ml of 6 M $HClO_4$, the solution was concentrated to ~5 ml. Upon cooling, red-violet crystals came out. After the product had been placed in a refrigerator overnight, the crystals were collected and then recrystallized from 15 ml of warm water with the addition of a few drops of 6 M $HClO_4$. Yield, 0.4 g.

Found: C, 31.95; H, 5.34; N, 10.37%. Calcd for [Co(*i*-DTMA)(acac)]ClO_4=$CoC_{11}H_{21}O_8N_3Cl$ (417.69): C, 31.63; H, 5.07; N, 10.06%.

(8) mer (N)-*Acetylacetonato(4-diethylenetriaminemonoacetato)-cobalt(III) Perchlorate,* mer(N)-*[Co(*i-*DTMA)(acac)]ClO$_4$*: The filtrate separated from the crude *fac*(*N*)-isomer in the above preparation (~4 ml) was concentrated to ~2 ml and then placed in a refrigerator overnight. A red precipitate, which was clearly different from the red-violet product (7), thus appeared. The precipitate was recrystallized from 5 ml of warm water with the addition of a few drops of 6 M $HClO_4$. Yield, 0.1 g.

Found: C, 31.62; H, 5.19; N, 10.16%. Calcd for [Co(*i*-DTMA)(acac)]ClO_4=$CoC_{11}H_{21}O_8N_3Cl$ (417.69): C, 31.63; H, 5.07; N, 10.06%.

(9) Bromination of the Acetylacetonato Complexes: The *fac*(*N*)-isomer of the acetylacetonato complex (0.3 g) was dissolved in 50 ml of an ethanol(50%)–water mixture, and then 0.15 g of *N*-bromosuccinimide was stirred in. The mixture was concentrated to 10 ml at ~50 °C with the aid of an air stream blown onto the surface. A brownish red precipitate came out as the evaporation proceeded. After the product had been cooled at 0 °C for 1 hr, the precipitate was collected and recrystallized from 10 ml of warm water with the addition of a few drops of 6 M $HClO_4$. Yield, 0.1 g.

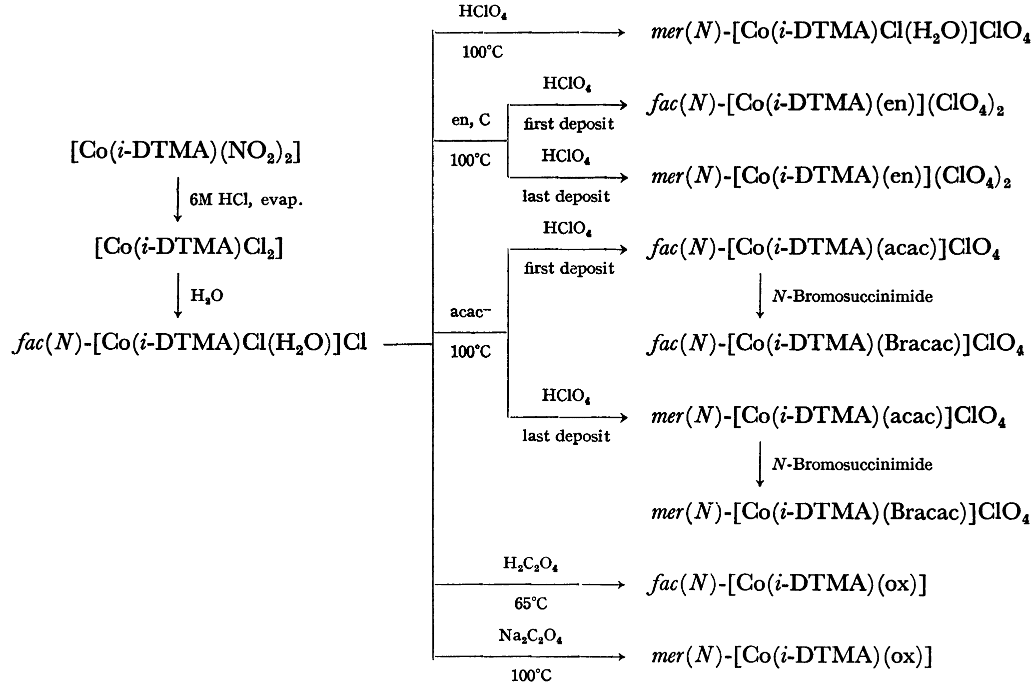
The *mer*(*N*)-isomer of the acetylacetonato complex was treated similarly. The yield of the bright red product was also 0.1 g.

Found: C, 26.34; H, 4.19; N, 8.41% for the brownish red isomer. C, 26.50; H, 4.18; N, 8.41% for the bright red isomer. Calcd for [Co(*i*-DTMA)(Bracac)]ClO_4=$CoC_{11}H_{20}O_8N_3ClBr$ (496.59): C, 26.60; H, 4.06; N, 8.46%.

Results and Discussion

Preparation. The preparation routes in this study are shown schematically in Table 1. Schneider and Collman[1)] obtained the dichloro complex, [Co(*i*-DTMA)Cl_2], by the evaporation of a suspension of the dinitro complex in concentrated hydrochloric acid, followed by the addition of ethanol. The evaporation product of the dinitro complex in our procedure probably consisted of the same dichloro complex as that of the pioneers. According to our experiment, however, the composition of the material is indefinite to some extent, since it changes quickly in the presence of moisture. The addition of a small amount of water

TABLE 1. PREPARATION SCHEME OF Co(III)-*i*-DTMA COMPLEXES



to the product, as has been described above, gives a satisfactory precipitate of the first aquation product from the dichloro complex, $[Co(i\text{-}DTMA)Cl(H_2O)]Cl\cdot H_2O$. The isolated solid is not hygroscopic at all, since it came out of the aqueous medium. The yield is nearly quantitative. It reacts with various anions and molecules to form substitution products. Therefore, it is a suitable starting substance for the preparation of the complexes of the series.

As has been described in the introduction, *i*-DTMA may coordinate with two different modes in octahedral complexes; judging from the results of Schneider and Collman,[1] the *fac*(*N*)-mode is considered to be more stable and/or to be easier to arise. Therefore, it was presumed that a high temperature was necessary for a *fac*(N)-isomer to isomerize to a *mer*(N)-isomer. It was also presumed that basic media were preferable for the isomerization, since the substitution and isomerization reactions of cobalt(III) complexes proceed faster in basic solutions than in acidic solutions.[5] Preparations were attempted on these assumptions; they were confirmed, at least qualitatively, as will be shown below.

In the preparation of the oxalato complexes, the red *mer*(*N*)-isomer, which will be identified in the following sections, occurred predominantly by means of the reaction between the starting complex and sodium oxalate at ~100 °C. On the other hand, the reaction with oxalic acid at ~65 °C produced the red-violet *fac*(*N*)-isomer. The use of sodium oxalate at ~65 °C also produced the red-violet isomer at first, but it turned to red after having been long kept at that temperature. These facts are consistent with the above assumptions. In the preparation of the ethylenediamine and the acetylacetonato complexes, two isomers of each complex were separated from the products obtained by the reactions at ~100 °C. It was observed that the yields of the *mer*(*N*)-isomers were extremely low when the reactions were performed at ~65 °C. These facts also confirm the assumptions.

The bromination of the acetylacetonato complexes at the central methine of the ligand was easily accomplished by the action of *N*-bromosuccinimide. This is in contrast with the fact that the acetylacetonatobis(ethylenediamine)cobalt(III) ion, $[Co(acac)(en)_2]^{2+}$, is not brominated even under forcing conditions.[6] On the other hand, there is much information indicating that tris(acetylacetonato)cobalt(III) and many analogues of the other metal ions, such as Cr(III), undergo bromination at the site.[7] Thus, the results indicate that the electrophilic substitution suffers an influence by the kinds of ligands which coordinate to the metal together with the reacting acetylacetonate.

Proton NMR Spectra. In the case of the coordination with the *mer*(*N*)-mode of the tetradentate, one ethylene bridge is forced to the δ and the other, to the λ conformation, and the out-of-plane glycinate ring skeleton must be planar. The oxalate and the acetylacetonate rings are considered to be planar, since these rings in many metal complexes have been confirmed to be planar by X-ray crystallographic analysis.[8] Therefore, the *mer*(*N*)-isomers of the oxalato and the acetylacetonato complexes possess a plane of symmetry; they belong to the C_s point group. On the other hand, the *fac*(*N*)-isomers have no element of symmetry; they belong to the C_1 point group. In the case of the ethylenediamine complex, neither isomer has an element of symmetry; since the conformation of the bidentate is not planar but *gauche*. However, the δ and the λ conformations of the bidentate give rise to no intrinsic difference in the *mer*(*N*)-isomer; the plane coplanar with the glycinate ring in the isomer may thus be taken as approximately a plane of symmetry.

Table 2. Resonances in the PMR spectra indicating the structure of some Co(III)-*i*-DTMA complexes (ppm downfield referred to *tert*-butyl alcohol as zero)

	CH (in acac)	CH_2 (in glycinate ring)	CH_3 (in acac)
fac(*N*)-[Co(*i*-DTMA)Cl(H_2O)]Cl	—	3.08, 2.91, 2.46, 2.29	—
mer(*N*)-[Co(*i*-DTMA)Cl(H_2O)]ClO_4	—	2.57	—
fac(*N*)-[Co(*i*-DTMA)(en)]$(ClO_4)_2$	—	3.19, 3.02, 2.78, 2.61	—
mer(*N*)-[Co(*i*-DTMA)(en)]$(ClO_4)_2$	—	2.79	—
mer(*N*)-[Co(*i*-DTMA)(ox)]	—	2.66	—
fac(*N*)-[Co(*i*-DTMA)(acac)]ClO_4	4.55	3.29, 3.12, 2.45, 2.28	1.00, 0.98
fac(*N*)-[Co(*i*-DTMA)(Barcac)]ClO_4	—	(3.29, 3.12, 2.45, 2.28)[a]	1.33, 1.31
mer(*N*)-[Co(*i*-DTMA)(acac)]ClO_4	4.50	2.70	0.99, 0.87
mer(*N*)-[Co(*i*-DTMA)(Bracac)]ClO_4	—	2.70	1.35, 1.22

a) The resonances of the glycinate ring protons of *fac*(*N*)-[Co(*i*-DTMA)(Bracac)]ClO_4 were not so clear because of the solubility limitation, but they were detectable by the comparison with the spectrum of the unbrominated complex. The spectrum of *fac*(*N*)-[Co(*i*-DTMA)(ox)] was not obtained owing to its low solubility.

Because of the symmetry described above, the glycinate ring protons in the *mer*(*N*)-isomers are exactly or approximately equivalent; hence, a singlet absorption due to the protons can be expected for the isomers. On the other hand, an AB quartet absorption is expected for the protons of the *fac*(*N*)-isomers. Thus, the PMR spectra make possible a decisive conclusion as to the structure of the complexes. Table 2 shows the observed resonances, which indicate the structure and composition. As may be seen there, one of the isomers of each complex exhibits a sharp singlet, and the other, a quartet, in the region of the glycinate absorption (around 3 ppm). The coupling constants, J_{AB}, of the latter are 17 Hz, in agreement with those obtained for other cobalt(III) complexes with a similar ring arrangement.[3] The coordination modes of the tetradentate in the isomers were, thus, assigned as has been indicated in the preceding section on preparation. It was observed that the absorption due to the methine proton of the acetylacetonato complexes (~4.5 ppm) disappeared completely in the spectra of the brominated products. This fact supports the actual bromination at the site of the ligand.

Electronic Absorption Spectra. Figures 2—5 show the visible and ultraviolet absorption spectra of the complexes studied, while the numerical values of the absorption maxima are summarized in Table 3.

As may be seen in Fig. 2, one of the chloroaquo complexes shows an intense first band with no distinct split, whereas the other shows a large split in the band. Such a large difference between their spectra cannot be expected if the tetradentate coordinates with the

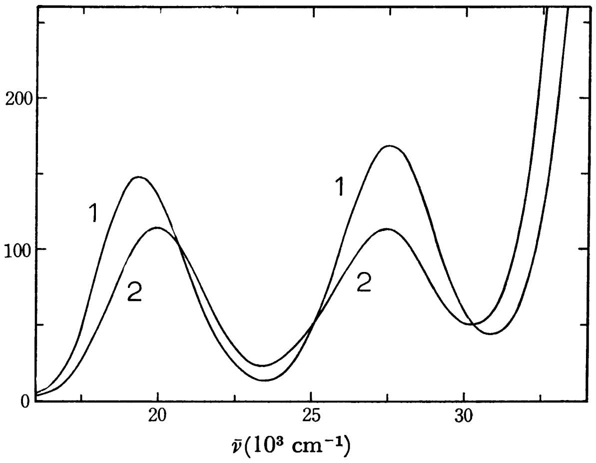


Fig. 3. Absorption spectra of *fac*(*N*)- and *mer*(*N*)-[Co(*i*-DTMA)(ox)].
1: the *fac*(*N*)-isomer; 2: the *mer*(*N*)-isomer

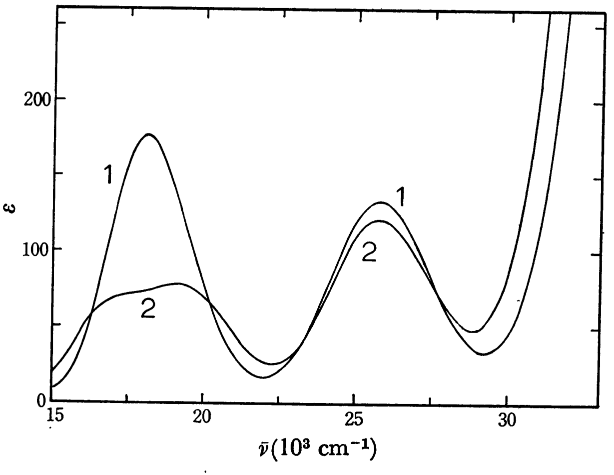


Fig. 2. Absorption spectra of *fac*(*N*)-[Co(*i*-DTMA)-Cl(H_2O)]Cl (1) and *mer*(*N*)-[Co(*i*-DTMA)Cl(H_2O)]-ClO_4 (2).

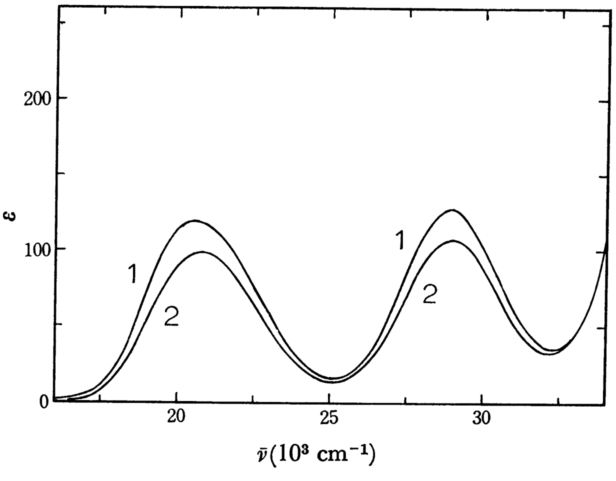


Fig. 4. Absorption spectra of *fac*(*N*)- and *mer*(*N*)-[Co(*i*-DTMA)(en)]$(ClO_4)_2$.
1: the *fac*(*N*)-isomer; 2: the *mer*(*N*)-isomer

TABLE 3. ABSORPTION MAXIMA OF THE ELECTRONIC SPECTRA OF SOME Co(III)-*i*-DTMA COMPLEXES

	I $\bar{\nu}$ (10^3 cm^{-1}) (ε) Ia	Ib	II or Sp $\bar{\nu}$ (10^3 cm^{-1}) (ε)
fac(*N*)-[Co(*i*-DTMA)Cl(H_2O)]Cl	18.08 (176.6)		25.77 (134.0)
mer(*N*)-[Co(*i*-DTMA)Cl(H_2O)]ClO_4	17 (sh)	19.08 (78.0)	25.71 (121.3)
fac(*N*)-[Co(*i*-DTMA)(en)]$(ClO_4)_2$	20.53 (119.8)		28.99 (127.8)
mer(*N*)-[Co(*i*-DTMA)(en)]$(ClO_4)_2$	20.75 (98.6)		28.99 (108.0)
fac(*N*)-[Co(*i*-DTMA)(ox)]	19.31 (148.0)		27.55 (168.4)
mer(*N*)-[Co(*i*-DTMA)(ox)]	19.92 (114.2)		27.40 (113.8)
fac(*N*)-[Co(*i*-DTMA)(acac)]ClO_4	18.98 (167.6)		30.77[a] (3880)
mer(*N*)-[Co(*i*-DTMA)(acac)]ClO_4	19.84 (156.6)		30.49[a] (4100)
fac(*N*)-[Co(*i*-DTMA)(Bracac)]ClO_4	19.01 (181.0)		29.20[a] (3760)
mer(*N*)-[Co(*i*-DTMA)(Bracac)]ClO_4	19.84 (178.0)		28.90[a] (3900)

a) Ligand specific band.

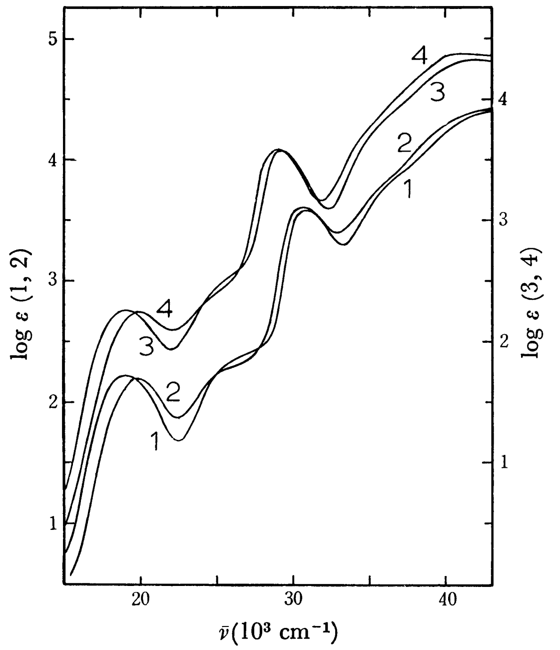


Fig. 5. Absorption spectra of [Co(*i*-DTMA)(acac)]ClO_4 and [Co(*i*-DTMA)(Bracac)]ClO_4.
1: the *fac*(*N*)-isomer of the acetylacetonato complex
2: the *mer*(*N*)-isomer of the acetylacetonato complex
3: the *fac*(*N*)-isomer of the bromoacetylacetonato complex
4: the *mer*(*N*)-isomer of the bromoacetylacetonato complex

same mode in both isomers. Therefore, it can reasonably be inferred from the spectra and the possible four configurations that the former is the *fac*(*N*)-isomer, while the latter is the *mer*(*N*)-isomer, which is in agreement with the assignment from the PMR spectra. It is not known, however, which of the residual coordination sites (1 and 2 in Fig. 1) the chlorine atom occupies in each isomer.

The oxalato and the acetylacetonato complexes are of the [CoN_3O_3] type, and there is much information about the spectra of this type of complex, *e.g.* [Co-$(gly)_3$].[9] There is a general trend for the *fac*-isomer to exhibit a more intense first band with no distinct split, whereas the *mer*-isomer exhibits a less intense first band with a wider band width or a deformation from the symmetrical shape. The configurations of the isomers were assigned on the basis of this trend, as has been indicated in the Preparation section, in agreement with the assignment based on the PMR spectra. These assignments are also consistent with the observation of the preparations, in which the *mer*(*N*)-isomers, the species considered to be difficult to produce, occurred at high temperatures.

It can be found that some regularities are present among the spectra of the acetylacetonato and the bromoacetylacetonato complexes. First, the bromination hardly affects the wave number of the first band, but slightly increases the intensity of the band. Second, the ligand specific band shifts to a lower wave number with the slight decrease in intensity by the bromination. It can be concluded from the spectral observations that the *fac*(*N*)- and *mer*(*N*)-configurations of each isomer of the acetylacetonato complex are mostly retained during the brominating reaction under the conditions used in the experiments.

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