Studies of the Cobalt(III) Complexes of 8-Amino-3,6-diazaoctanate Ion. II.[1] The Preparation and Some Properties of the Complexes with a Carbonate, Oxalate, or Malonate Ligand

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The following new cobalt(III) complexes containing the quadridentate 8-amino-3,6-diazaoctanate ion (adao) have been prepared: α-[Co(adao)(ox)], α-[Co(adao)(mal)] (mal, malonate ion), *β-mer(N)*-[Co(adao)(CO_3)], *β-mer(N)*-[Co(adao)(mal)], *β-fac(N)*-[Co(adao)(CO_3)], *β-fac(N)*-[Co(adao)(ox)], and *β-fac(N)*-[Co(adao)(mal)]. The geometrical isomers have been separated by the chromatographic technique. The configurations of the complexes have been identified by means of the electronic absorption spectra and the proton NMR spectra.

The 8-amino-3,6-diazaoctanate ion (adao)* can coordinate with four coordination modes in an octahedral complex, as is shown in Fig. 1-a. These modes were designated as *α,β-mer(N)*, *β-fac(N)*, and *trans* by Schneider and Collman.[2] The two optical isomers (*Δ* and *Λ*) which arise from the contribution of a configurational chirality may exist in each of three coordination modes (*α,β-mer(N)*, and *β-fac(N)*) of their four coordination modes. When we consider the configuration of the secondary amine nitrogen atom (*s*-N) in adao, further discrimination is possible in the *β-mer(N)*, *β-fac(N)*, and *trans* forms. This is illustrated in Fig. 1-b. The configuration of the chiral *s*-N atom is described by the *R* or *S* rule proposed by Cahn, Ingold, and Prelog.[3] For the respective *β-mer(N)*, *β-fac(N)*, and *trans* racemic isomers, the existence of isomers, (*SR,RS*) and (*SS,RR*), is possible. However, such isomers are impossible to exist for the α racemic isomer. Thus, five geometrical isomers *α,β-mer(N)*-(*SR,RS*), *β-mer(N)*-(*SS, RR*), *β-fac(N)*-(*RS,SR*), and *β-fac(N)*-(*RR,SS*), are possible when a symmetrical bidentate ligand occupies the residual sites.

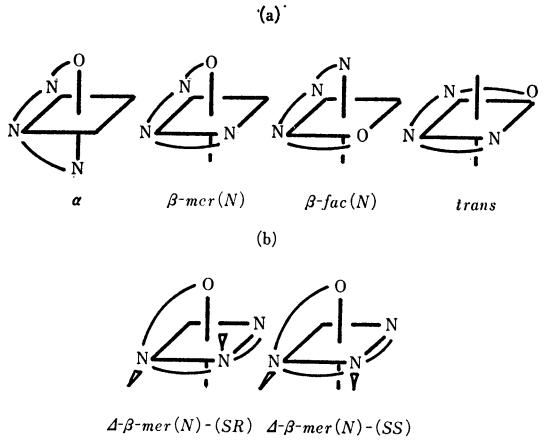

Fig. 1. Coordination modes of adao (a) and configurations around the *s*-N of adao in *Δ-β-mer(N)* coordination mode (b).

* The following abbreviations are used for the ligands: adao, 8-amino-3,6-diazaoctanate; edda, ethylenediamine-*N,N'*-diacetate; ed3a, ethylenediamine-*N,N,N'*-triacetate; *i*-dtma, 4-diethylenetriaminemonoacetate; ox, oxalate; mal, malonate.

If an unsymmetrical bidentate ligand occupies, the number of the isomers increase. Schneider *et al.*,[2] Fukuhara *et al.*,[4] and the present author[1] have studied the cobalt(III) complexes containing the quadridentate ligand. It was shown in these studies that most complexes isolated were the *β-mer(N)* isomers, although the existence of the α and the *β-fac(N)* isomers is also to be expected. In order to clarify this problem, the isolation of the isomers with a symmetrical bidentate ligand was attempted. Thus, we succeeded in isolating some of the α and *β-fac(N)* isomers for the carbonato, oxalato, and malonato complexes.

Experimental

Materials. Diethylenetriamine (Nakarai Chemicals), oxalic acid, malonic acid and all the other reagent-grade chemicals were used without further purification. Column chromatography was carried out by the use of Dowex 50 W-X8 cation-exchange resin.

Preparations. (1) *Isomers of (8-Amino-3,6-diazaoctanato)-carbonatocobalt(III)*, [*Co(adao)(CO_3)*]: The carbonato complex (5 g), which had been isolated by the method of Schneider *et al.*,[2] was dissolved in 30 cm^3 of water. The solution was then poured into a column (50 mm × 350 mm) containing Dowex 50W-X8 (200—400 mesh, sodium form). By elution with water, the adsorbed bands were gradually separated into two bands: the first was dark-red (Eluate I, ≈100 cm^3), and the second was red-violet (Eluate II, ≈300 cm^3). Eluate I was concentrated to about 15 cm^3 in a rotary evaporator below 40 °C and then kept in a refrigerator for two days. The red precipitate thus deposited (Precipitate I) was collected. Although it is possible to obtain the considerable precipitate from the mother filtrate, the precipitate does not consist of only one isomer. Precipitate I was recrystallized from warm water (≈3 cm^3, 65 °C) and subsequently washed with ethanol and ether. Yield, 0.25 g. Eluate II was reduced to about 5 cm^3 in a rotary evaporator, and then concentrated to nearly dryness over silica gel in a vacuum desiccator. The red-violet deposit was collected and recrystallized from 1 cm^3 of warm water. It was washed with ethanol and acetone. Yield, 0.12 g.

(2) *Isomers of (8-Amino-3,6-diazaoctanato)oxalatocobalt(III)*, [*Co(adao)(ox)*]: A solution of oxalic acid dihydrate (0.6 g) in 5 cm^3 of warm water (≈55 °C) was added to a suspension of Schneider's carbonato complex, [Co(adao)(CO_3)], (1.4 g) in 15 cm^3 of water, and then the mixture was heated at ≈75 °C for 4 h with continuous stirring. To the resulting product, which contained an appreciable amount of a precipitate, was added 40 cm^3 of water, and the precipitate was dissolved by

heating (≈70 °C). The solution was cooled, and then it was filtered. The red filtrate was poured into a column (20 mm × 700 mm) containing Dowex 50 W-X8 (100—200 mesh, hydrogen form), and the adsorbed sustance was eluted with water. The red band which was adsorbed at the top of the column, separated cleanly into three bands with red, pink-red, and red-violet color in the order of the elution. Each of three eluates (≈100 cm³, ≈100 cm³, and ≈120 cm³) was concentrated to about 5 cm³ in a rotary evaporator at ≈55 °C, and then cooled. Each deposit was recrystallized from hot water (5—7 cm³, ≈70 °C) and was washed with methanol and ether. The yields were 1.0 g for the red, 0.05 g for the pink-red, and 0.05 g for the red-violet isomer.

(3) *Isomers of (8-Amino-3,6-diazaoctanato)malonatocobalt(III), [Co(adao)(mal)]*: The reaction product was obtained and separated by a similar procedure to that described in (2) using malonic acid instead of oxalic acid. When three elutes (≈300 cm³, ≈250 cm³, and ≈300 cm³) were concentrated to dryness, dark-red, pink-red, and red-violet products were obtained respectively. Each product was washed with acetone. The pink-red product was hygroscopic; hence, it was difficult to handle. The yields were 1.0 g for the dark-red, 0.05 g for the pink-red, and 0.1 g for the red-violet isomer. The red-violet isomer can be obtained in a better yield by the reaction at a higher temperature (≈80 °C), but the yield of the pink-red isomer decreases.

Measurements. The visible and ultraviolet absorption spectra were measured with a Hitachi EPS-3T Recording Spectrophotometer or a Shimadzu UV-200 Recording Spectrophotometer. The proton NMR spectra were recorded with a Varian XL-100 spectrometer in deterium oxide, with *t*-butyl alcohol as the internal reference.

Results and Discussion

The analytical data for the complexes prepared are summarized in Table 1.

Electronic Spectra. The electronic spectra are shown in Figs. 2—4, while the numerical values of the absorption maxima are summarized in Table 2. If the configuration of the ligating nitrogen atom of adao is not considered, three geometrical isomers (*α,β-mer(N)*, and *β-fac(N)*) are possible for the complexes of [Co(adao)(AA)] (AA=CO_3, ox, and mal). The *α* and the *β-fac(N)* isomers belong to a *fac* type of $[CoN_3O_3]$, and the *β-mer(N)* to a *mer* one. As regards the complex of $[CoN_3O_3]$ type, it is well known that the first band of the *mer* isomer is broader than that of the *fac* isomer.[5] As may be seen in Fig. 3, which shows the spectra of the oxalato complexes, the first band of the red isomer is broader than those of the other two. From this spectral difference, the red isomer is identified as having the *β-mer(N)* structure. Although the two remaining isomers must belong to the *fac* isomer, it is difficult to determine their structures on the basis of the spectral data alone. However, it is observed that the absorption intensity of the first band of the red-violet isomer is stronger than that of the pink-red one. Similar features are observed among the spectra of the malonato com-

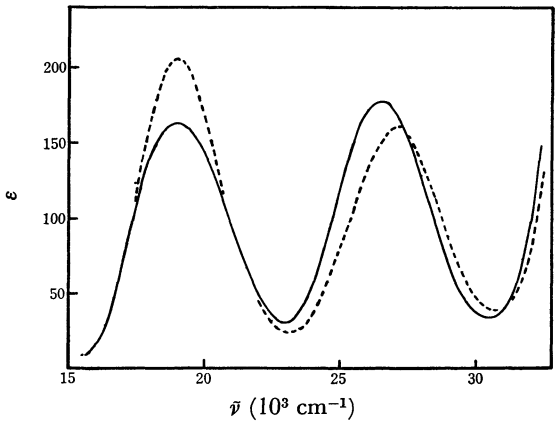

Fig. 2. Absorption spectra of [Co(adao)(CO_3)] complexes.
——: *β-mer(N)*-[Co(adao)(CO_3)] (red),
------: *β-fac(N)*-[Co(adao)(CO_3)] (red-violet).

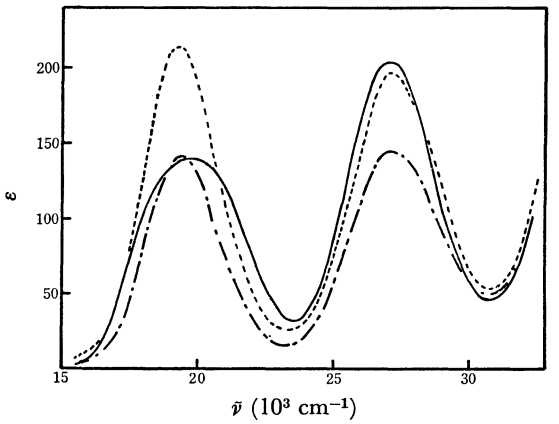

Fig. 3. Absorption spectra of [Co(adao)(ox)] complexes.
-·-·-: α-[Co(adao)(ox)] (pink-red),
——: *β-mer(N)*-[Co(adao)(ox)] (red),
------: *β-fac(N)*-[Co(adao)(ox)] (red-violet).

Table 1. Elemental analyses

	Color	C (%)		H (%)		N (%)	
		Found	Calcd	Found	Calcd	Found	Calcd
α-[Co(adao)(ox)]·1.5H_2O	Pink-red	29.06	28.75	4.85	5.13	12.50	12.57
α-[Co(adao)(mal)]·0.5H_2O	Pink-red	32.75	32.74	5.10	5.19	12.44	12.73
β-mer(N)-[Co(adao)(CO_3)]·H_2O	Red	28.14	28.29	5.43	5.43	14.25	14.14
β-mer(N)-[Co(adao)(ox)]	Red	30.98	31.28	4.61	4.59	13.51	13.68
β-mer(N)-[Co(adao)(mal)]·2.5H_2O	Dark-red	29.71	29.52	5.76	5.78	11.50	11.47
β-fac(N)-[Co(adao)(CO_3)]·2H_2O	Red-violet	26.39	26.68	5.78	5.76	13.25	13.33
β-fac(N)-[Co(adao)(ox)]	Red-violet	31.07	31.28	4.65	4.59	13.51	13.68
β-fac(N)-[Co(adao)(mal)]·0.5H_2O	Red-violet	33.16	32.74	5.14	5.19	13.13	12.73

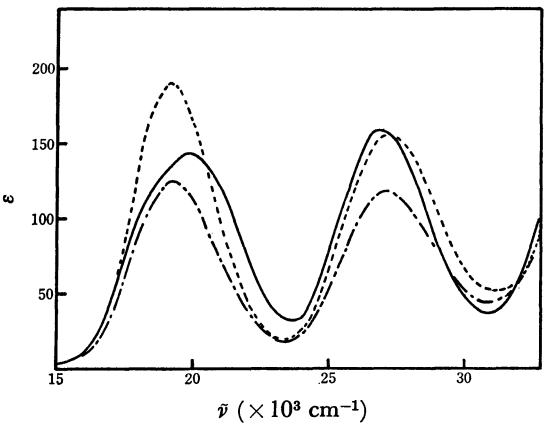

Fig. 4. Absorption spectra of [Co(adao)(mal)] complexes.
-·-·-: α-[Co(adao)(mal)] (pink-red),
——: *β-mer(N)*-[Co(adao)(mal)] (dark-red),
------: *β-fac(N)*-[Co(adao)(mal)] (red-violet).

TABLE 2. ABSORPTION DATA OF THE adao-Co(III) COMPLEXES (Wave numbers are in 10^3 cm^{-1})

	Color	I $\bar{\nu}_{max}$ (ε)	II $\bar{\nu}_{max}$ (ε)
α-[Co(adao)(ox)]	Pink-red	19.30(142)	27.10(145)
α-[Co(adao)(mal)]	Pink-red	19.23(125)	27.06(118)
β-mer(N)-[Co(adao)-(CO_3)]	Red	19.00(162)	26.39(177)
β-mer(N)-[Co(adao)-(ox)]	Red	≈19.9 (140)	27.03(204)
β-mer(N)-[Co(adao)-(mal)]	Dark-red	≈19.9 (143)	27.00(160)
β-fac(N)-[Co(adao)-(CO_3)]	Red-violet	19.00(206)	27.10(160)
β-fac(N)-[Co(adao)-(ox)]	Red-violet	19.23(213)	27.17(196)
β-fac(N)-[Co(adao)-(mal)]	Red-violet	19.12(190)	27.17(155)

plexes (Fig. 4), and it is inferred that the dark-red isomer is the *β-mer(N)*, while the pink-red and red-violet ones are the α or the *β-fac(N)*. Among the isomers of the carbonato complex, it is found that the intensity of the first band of the red-violet isomer is stronger and narrower than that of the red one.

Proton NMR Spectra. The proton NMR spectra of the two isomers of the carbonato complex and the red isomer of the oxalato complex are shown in Fig. 5. The PMR spectra of the dark-red and red-violet isomers of the malonato complex are shown in Fig. 6. It was difficult to measure the spectra of the other two isomers of the oxalato complex because of their low solubilities. For the pink-red isomer of the malonato complex, the PMR spectrum was not obtained satisfactorily. As can be inferred from the coordination modes of adao in Fig. 1-a, these isomers may be classified into two groups from the standpoint of the disposition of adao's glycinate ring: one group consists of the isomers with out-of-plane glycinate (α and *β-mer(N)*), and the other, of those with in-plane glycinate (*β-fac(N)* and *trans*). Therefore, the PMR spectra of the former

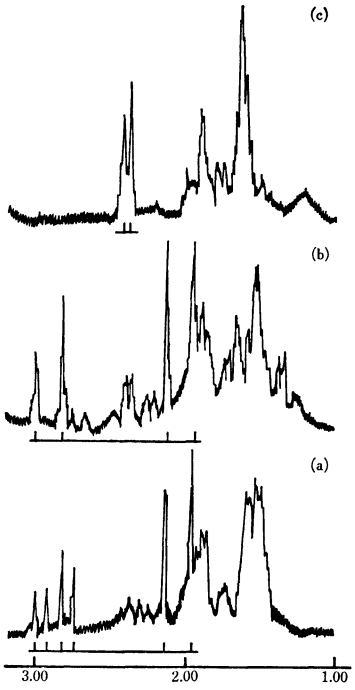

Fig. 5. Proton NMR spectra.
(a): *β-mer(N)*-[Co(adao)(ox)](red),
(b): *β-mer(N)*-[Co(adao)(CO_3)] (red),
(c): *β-fac(N)*-[Co(adao)(CO_3)](red-violet).

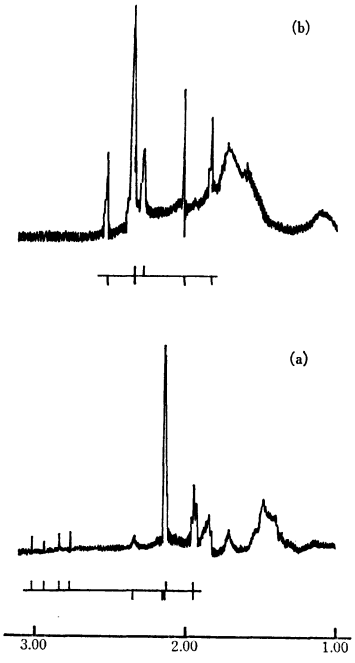

Fig. 6. Proton NMR spectra.
(a): *β-mer(N)*-[Co(adao)(mal)] (dark-red),
(b): *β-fac(N)*-[Co(adao)(mal)] (red-violet).

isomers may be expected to be different from those of the latter isomers at the resonances of the glycinate protons. It has been reported that a considerable difference exists between the isomers of [Co(edda)-(AA)][1±] (AA=$(NH_3)_2$, en, ox, and mal)[6] and

$[Co(adao)(AA)]^{2+}$ ($AA=(NH_3)_2$, en)[1]; that is, a AB quartet appears for the out-of-plane ring (R-ring) protons and an apparent singlet for the in-plane ring (G-ring) protons. It has also been observed in the spectra of the edda and ed3a Co(III) complexes that the value of $\delta_{AB}(=\delta_A-\delta_B)$ for the R-ring protons is in the range of 0.7 to 1.0 ppm, while that for the G-ring protons is in the range of 0.0 to 0.4 ppm.[7] As may be seen in Fig. 5, the red isomer of the oxalato complex, which has been inferred to be the *β-mer(N)* structure on the basis of the electronic spectrum, shows one AB quartet in the range of 1.96 to 3.00 ppm, although the two resonances at the lower field split into doublet. A pair of doublets in the range of 2.74 to 3.00 ppm is considered to be due to the coupling with the amine proton, which is not completely exchanged at the time of the measurement. The value of the δ_{AB} is about 0.76 ppm ($J_{AB}=18$ Hz).

The red isomer of the carbonato complex shows one clear AB quartet in the range of 1.94 to 3.00 ppm. The δ_{AB} is calculated to be 0.86 ppm. On the other hand, the red-violet isomer of the carbonato complex exhibits two resonances at 2.37 and 2.41 ppm. If it is assumed that the J_{AB} is 16 Hz,[8] the δ_{AB} is 0.12 ppm. From these spectral patterns, it can be found that the glycinate ring's disposition of the red isomer is out-of-plane, while that of the red-violet one is in-plane. Consequently, it is reasonable to assign the red isomer to the *β-mer(N)*, and the red-violet one, to the *β-fac(N)*.

The malonato isomers show more complicated spectra than those of the oxalato and carbonato isomers because of the existence of the malonate ring protons. For the dark-red isomer, it was found that the four peaks in the range of 2.77 to 3.02 ppm (Fig. 6-a) are reduced to two peaks upon the addition of Na_2CO_3 to the solution. Thus, the resonances of the dark-red malonato isomer consist of two AB quartets: one is the resonances centered at about 2.45 ppm and the other is those centered at 2.145 ppm. The δ_{AB} and J_{AB} of the quartet with the center at 2.45 ppm are 0.80 ppm and 18 Hz respectively. From the similarity of these values (δ_{AB} and J_{AB}) between the dark-red isomer and the *β-mer(N)*-ox isomer, this AB quartet is attributed to the glycinate protons of adao. The other quartet may be considered to be due to the methylene protons of the malonate ring. Therefore, the dark-red isomer is assigned to the *β-mer(N)*. The PMR spectrum of the red-violet isomer consists, in the lower field, of a doublet with the center at 2.32 ppm and a quartet with the center at 2.18 ppm. The δ_{AB} of the former is about 0.16 ppm and that of the latter, 0.48 ppm. The chemical shift and the δ_{AB} of the doublet of this isomer are similar to those of the *β-fac(N)* isomer of the carbonato complex. The quartet is obviously due to the malonate ring protons. From these facts, the red-violet isomer is assigned to the *β-fac(N)* structure.

The cobalt-malonate ring is six-membered and is necessarily conformationally bent: three conformations, chair, boat, and skew-boat, are possible. Buckingham *et al.*[9] proposed that the boat and skew-boat conformations are more stable than the chair one, on the basis of the theory in which the dipole interaction between electron pairs on the ligating oxygen and on the adjacent carbonyl oxygen is more important in the chair form. Moreover, they suggested that the skew-boat conformation is more stable than the boat one, when there is interaction between the malonate hydrogen atom and another ligating group. The theory and the results of the PMR spectra indicated that the malonate rings in the complex ions such as $[Co(mal)(en)_2]^+$ and $[Co(mal)_2(en)]^-$ take the skew-boat conformation. On the other hand, when the absolute configuration of $(-)_{589}$-Na$[Co(mal)_2(en)]$ was studied by Butler and Snow by the X-ray method, they showed that the malonate rings in the complex ion adopt the boat conformation.[10] Furthermore, Matsumoto and Kuroya, in investigating the crystal structure of $(-)_{589}$-$[Co(NO_2)_2(en)_2]\cdot(+)_{589}$-$[Co(mal)_2(en)]$ by the X-ray method, showed that the two malonate rings are nearly planar.[11] From these facts and the theory proposed by Buckingham *et al.*, the existence of the chair conformers seems to be impossible for the Co(III)-complex with the malonate ring. When the molecular models of the *β-mer(N)*-[Co(adao)(mal)] isomer are examined, it seems to be impossible that the malonate ring takes the boat conformation because of the interactions between the malonate hydrogen atoms and the adao's NH and NH_2 hydrogen atoms.

Three conformations, boat, skew-boat, and planar, are possible for the *β-fac(N)*-[Co(adao)(mal)]. When the symmetry of only the malonate ring is considered, the chemical environments of two malonate hydrogen atoms are equivalent in the skew-boat and the planar conformation, but not in the boat one. Therefore, it may be expected that the δ_{AB}'s of the malonate protons for the formers are smaller than that for the latter. As may be seen in Fig. 6, the δ_{AB} of the malonate protons of the *β-fac(N)* isomer is larger than that of the *β-mer(N)* isomer. Consequently, it may be inferred that the malonate chelate ring in the *β-mer(N)* isomer adopts the skew-boat or the planar conformation and that in the *β-fac(N)* isomer the boat one.

The possible existence of the two *β-mer(N)* isomers arising from the configuration of *s*-N atom of adao is shown in Fig. 1-b. From the examination of molecular models, it may be expected that the PMR spectrum of *β-mer(N)*-(*SR,RS*) isomer is different from that of the *β-mer(N)*-(*SS,RR*) at the resonances of the glycinate ring protons. Thus, if the *β-mer(N)* complex isolated is a mixture, a pair of doublet at the high field portion of the AB quartet pattern may be observed in the PMR spectrum. However, the PMR spectrum with a pair of doublet at the region mentioned above, is not obtained. Thus, the PMR evidences indicate that the respective *β-mer(N)* complexes isolated consist of one configuration for *s*-N atom of adao. However, it is difficult to assign the configuration of the *s*-N on the basis of the PMR spectra. On the other hand, the examination of molecular models for the two possible *β-fac(N)* isomers shows that the *β-fac(N)*-(*RS,SR*) configuration is more favoured than the *β-fac(N)*-(*RR,SS*), because the latter configuration exhibits the interaction between the hydrogen atom of the glycinate ring and the terminal amino hydrogen atom of adao. Furthermore, the PMR

spectrum shows only one clear doublet pattern. Thus, it may be inferred that the *β-fac(N)* isomers prefer the *(RS,SR)* configuration.

Besides the well-known *β-mer(N)* coordination mode, the α and the *β-fac(N)* modes are established for the oxalato and malonato complexes. Although the configuration (whether *(SR,RS)* or *(SS,RR)*) of the *s*-N in the *β-mer(N)* isomers can not be decided, it is found that the *β-mer(N)* complex isolated in this work adopts only one of the two configurations. For the malonate complexes, it is difficult to decide the ring conformation exactly. It has been inferred, however, that the conformation is the skew-boat in the *β-mer(N)* isomer and the chair in the *β-fac(N)* one. From Table 2, it may be seen that the apparent maximum of the first absorption band in the *β-mer(N)* isomer is at the same or a higher wave number than those in the corresponding α and *β-fac(N)* isomers. It was found that there are some differences in the absorption and PMR spectra between the author's *β-mer(N)*-carbonato complex and Collman's. Also, the carbonato complex isolated by Collman's method was separated cleanly into two bands by the chromatography. These facts suggest that Collman's *β-mer(N)*-carbonato complex contained another species. It is noticeable that the second band maximum of the author's *β-mer(N)* carbonato isomer is at considerably the lower wave number than that of the *β-fac(N)* one. Such difference in the second band maxima between isomers of $[CoN_3O_3]$ type have not been recognized previously,[5,12] although it has been reported that the second band of the *mer(trans)*-$[Co(CO_3)(gly)(NH_3)_2]$[13] or *mer(N)*-[Co(*i*-dtma)(CO_3)][14] exhibits a splitting.

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