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Studies of the Cobalt(III) Complexes of 8-Amino-3,6-diazaoctanate Ion. III.[1] Preparations and Some Properties of Complexes with Chloro, Nitro, or Aqua Ligands

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The following new cobalt(III) complexes containing the 8-amino-3,6-diazaoctanate ion (adao)[2] have been prepared: α-[Co(adao)Cl_2], two isomers of *β-mer(N)*-[Co(adao)Cl_2], *β-fac(N)*-[Co(adao)Cl_2], α-[Co(adao)$(NO_2)_2$], two isomers of *β-mer(N)*-[Co(adao)$(NO_2)_2$], α-[Co(adao)$(H_2O)_2$]$(ClO_4)_2$, and *β-mer(N)*-[Co(adao)$(H_2O)_2$]$(ClO_4)_2$. The geometrical structures have been determined on the basis of the electronic spectra, the proton NMR spectra, and the deductions from their derivation processes.

Four geometrical isomers, α, *β-mer(N)*, *β-fac(N)*, and *trans*,[3] are possible in each [Co(adao)X_2] type complex (X=Cl^-, NO_2^-, or H_2O), as is shown in Fig. 1-a. 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* isomers (Fig. 1-b). Thus, seven racemic geometrical isomers, α-(*SR,RS*), *β-mer(N)-(RS,SR)*, *β-mer(N)-(RR,SS)*, *β-fac(N)-(RS,SR)*, *β-fac(N)-(SS,RR)*, *trans-(RS,SR)*, *trans-(SS,RR)*,[4] are possible when two same unidentate ligands occupy the residual sites. In a previous paper,[1] the present author reported that three geometrical isomers, α, *β-mer(N)*, and *β-fac(N)*, were isolated in each [Co(adao)(O–O)] type complex (O–O=CO_3^{2-}, ox, and mal). Also in the [Co(adao)X_2] type, the existence of other isomers than *β-mer(N)* is to be expected. However, only the existence of *β-mer(N)* coordination mode was suggested by Schneider *et al.*[3] Furthermore, their *s*-N configurations were not decided. In order to clarify this problem, the isolation of the isomers was attempted. Thus, the author succeeded in isolating some of α, *β-mer(N)*, and *β-fac(N)* isomers for the dichloro, dinitro, and diaqua complexes.

Experimental

Preparation of Ligand. 8-Amino-3,6-diazaoctanoic acid (Hadao) was prepared by modifying the method of Schneider and Collman.[3]

Preparations of Complexes. *(1) Crude-[Co(adao)*$(NO_2)_2$*]*: The crude dinitro complex was isolated by modifying the Collman's method.[3]

(2) Crude-[Co(adao)Cl_2*]*: The crude dichloro complex was prepared by modifying the Collman's method.[3]

(3) α-[Co(adao)Cl_2*]*: The treatment of the crude-[Co(adao)Cl_2] with $HClO_4$ gave *β-mer(N)*-[Co(adao)(Cl)(H_2O)]ClO_4. The detailed preparative procedure and the structural assignment will be described elsewhere. The resulting *β-mer(N)*-[Co(adao)(Cl)(H_2O)]ClO_4 (7.44 g) was added to 30 cm^3 of water containing Li_2CO_3 (2.22 g). The suspension was heated on a water bath at 80 °C for 4 h. After cooling, the resulting precipitate was removed by filtration. When the filtrate was concentrated on a water bath with an aid of air stream, red crystals began to deposit. After the product was cooled, the crystals were collected on a filter, and then washed with an ethanol–ether (1 : 1) mixture. The filtrate was concentrated again, and then the second precipitate was filtered off. To the remaining filtrate was added 5 cm^3 of 6 M (1 M=1 mol dm^{-3}) HCl. When the mixture was heated at about 65 °C in a water bath for 20 min, blue crystals began to appear. To the resulting product was poured 10 cm^3 of water, and the mixture was then cooled in an ice bath. The deep blue crystals precipitated were collected on a filter, and washed with water, ethanol, and ether, in turn. Yield, ≈0.3 g.

Found: C, 24.38; H, 4.97; N, 14.28%. Calcd for [Co(adao)Cl_2]=$CoC_6H_{14}N_3O_2Cl_2$: C, 24.85; H, 4.87; N,14.49%.

*(4) β-*mer*(N)-[Co(adao)*Cl_2*]*: *a)*: *β-mer(N)*-[Co(adao)Cl_2]·$2H_2O$ (violet gray); The crude dichloro complex (30 g) obtained in *(2)* was dissolved in 390 cm^3 of hot 2 M HCl (≈80 °C), and then the product was filtered. The filtrate was cooled in a refrigerator for 3 d. The crystals were collected on a filter, and washed first with ethanol, then with a mixture of ethanol and ether (1 : 1). Yield, ≈5 g.

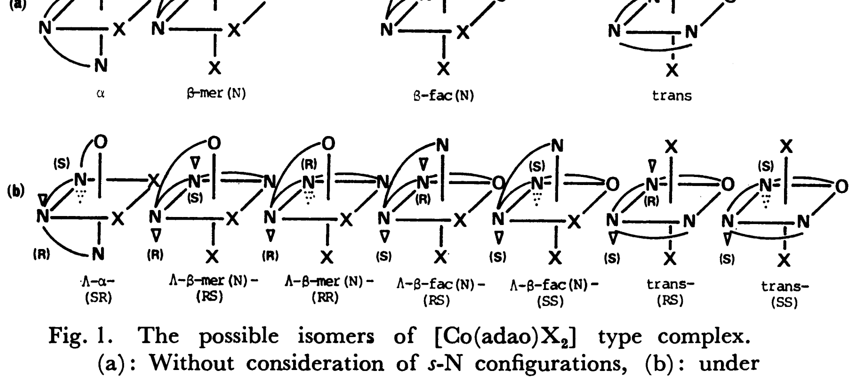

Fig. 1. The possible isomers of [Co(adao)X_2] type complex. (a): Without consideration of *s*-N configurations, (b): under consideration of *s*-N configurations.

Found: C, 22.40; H, 5.43; N, 13.18%. Calcd for $[Co(adao)Cl_2]\cdot 2H_2O = CoC_6H_{18}N_3O_4Cl_2$: C, 22.10; H, 5.56; N, 12.89%.

b): *β-mer(N)*-$[Co(adao)Cl_2]\cdot HCl\cdot 0.5H_2O$ (silver gray); The filtrate obtained in the previous procedure *(4-a)* was evaporated with an aid of air stream until silver gray crystals appeared. After cooling, the crystals were collected, and then washed with ethanol, a mixture of ethanol and ether (1 : 1), in turn. Yield, ≈15 g.

Found: C, 21.19; H, 4.95; N, 12.49%. Calcd for $[Co(adao)Cl_2]\cdot HCl\cdot 0.5H_2O = CoC_6H_{16}N_3O_{2.5}Cl_3$: C, 21.48; H, 4.81; N, 12.52%.

(5) β-fac(N)-[Co(adao)Cl$_2$]: *β-fac(N)*-$[Co(adao)(Cl)(H_2O)]ClO_4\cdot H_2O$ (0.26 g), of which preparative procedure will be described elsewhere, was suspended in 10 cm^3 of water. To the suspension, 2 cm^3 of 2 M HCl was added, and the mixture was heated until it dissolved. The resulting solution was concentrated to dryness on a water bath with an aid of air stream. After 5 cm^3 of water and 2 cm^3 of 2 M HCl were added to the concentrated product, the mixture was concentrated again, and then the product was allowed to stand at room temperature. The product was convered with 2 cm^3 of 2 M HCl, and then this mixture was evaporated to a half of its original volume. After the violet blue crystals were collected on a filter, they were washed with ethanol, and ether in this order. Yield, ≈0.1 g.

Found: C, 24.55; H, 4.64; N, 14.46%. Calcd for $[Co(adao)Cl_2] = CoC_6H_{14}N_3O_2Cl_2$: C, 24.85; H, 4.87; N, 14.49%.

(6) α-[Co(adao)(NO$_2$)$_2$]: To a solution of silver perchlorate (3 g) in 10 cm^3 of water, α-$[Co(adao)Cl_2]$ (1.45 g) was suspended, and then the suspension was heated at 60 °C for 10 min. During the reaction, silver chloride came out. After the reaction mixture had been cooled in an ice bath, the silver chloride was filtered off. The pink red filtrate was reduced in volume to about 2 cm^3 in a rotary evaporator below 40 °C, and then a small amount of 2 M NaBr solution was added until no more white crystals precipitated. After the silver bromide was removed by filtration, the filtrate was diluted to 10 cm^3 with water. To the solution, sodium nitrite (0.69 g) was added, and then the mixture was heated at 65 °C for 5 min. Orange crystals appeared. They were collected, and then washed with ethanol, and with ether. Yield, ≈0.6 g.

Recrystallization was carried out by means of fractional extraction with hot water (≈80 °C). The first extract (≈50 cm^3) was discarded. The crystals in the second and third extract (150 cm^3 respectively) consisted of only α-dinitro isomer. Yield, ≈0.3 g.

Found: C, 22.98; H, 4.60; N, 22.94%. Calcd for $[Co(adao)(NO_2)_2] = CoC_6H_{14}N_5O_6$: C, 23.16; H, 4.54; N, 22.51%.

(7) β-mer(N)-[Co(adao)(NO$_2$)$_2$]: Although the *β-mer(N)*-dinitro isomer had been separated by Schneider and Collman,[3] the present author found that the following procedure gave the *β-mer(N)* isomer in a higher purity. Furthermore, it was also found that there are two *β-mer(N)* dinitro isomers, namely one sparingly soluble isomer and another soluble one.

a): The sparingly soluble isomer with an orange yellow color; Sodium nitrite (0.7 g) and *β-mer(N)*-$[Co(adao)(Cl)(H_2O)]ClO_4$ (1.86 g) were added in 30 cm^3 of water, and the mixture was heated at 80 °C for half an hour with stirring. During this period, a large amount of orange yellow crystals appeared. After cooling, the crystals were collected on a filter, and washed with a mixture of ethanol and ether (1 : 1). The filtrate was reserved for the isolation of soluble isomer.

Recrystallization was carried out by the fractional extraction. The orange yellow crystals (1.2 g) were extracted with four 20 cm^3 portions of hot water (≈80 °C), and then 50 cm^3 one. The last main extract (≈50 cm^3) was cooled in an ice bath, then the orange yellow crystals were deposited. They were washed with ethanol, and with ether. Yield, ≈0.2 g.

Found: C, 23.07; H, 4.61; N, 22.28%. Calcd for $[Co(adao)(NO_2)_2] = CoC_6H_{14}N_5O_6$: C, 23.16; H, 4.54; N, 22.51%.

b): The soluble isomer with a yellow color; The reserved filtrate in *(7-a)* was allowed to stand at room temperature for 3 h, whereupon the yellow needles precipitated. When the yield of needles was very small, the filtrate was permitted to stand for 3 d. After filtration, the crystals were washed with an ethanol–ether (1 : 1) mixture. Yield, ≈0.1 g. They were recrystallized from 5 cm^3 of hot water.

Found: C, 23.02; H, 4.62; N, 22.54%. Calcd for $[Co(adao)(NO_2)_2] = CoC_6H_{14}N_5O_6$: C, 23.16; H, 4.54; N, 22.51%.

(8) α-[Co(adao)(H$_2$O)$_2$](ClO$_4$)$_2$·H$_2$O: In 3 cm^3 of water, α-$[Co(adao)(NO_2)_2]$ (0.15 g) was suspended, and then to the suspension, 3 cm^3 of 6 M $HClO_4$ was added dropwise. The mixture was heated at 80 °C about 10 min. The resulting solution with a red orange color was concentrated on a water bath under an air stream. The color of solution changed to a red one. The concentrated solution was cooled, and then filtered. After ethanol (30 cm^3) was added to the filtrate, ether (150 cm^3) was poured to it. When the mixture was cooled in an ice bath, pink crystals appeared. The crystals were collected on a filter, and washed with ethanol, and then stored over silica gel in a desiccator. Yield, ≈0.05 g.

Found: C, 15.53; H, 4.36; N, 8.96%. Calcd for $[Co(adao)(H_2O)_2](ClO_4)_2\cdot H_2O = CoC_6H_{20}N_3O_{13}Cl_2$: C, 15.27; H, 4.27; N, 8.90%.

(9) β-mer(N)-[Co(adao)(H$_2$O)$_2$](ClO$_4$)$_2$·H_2O: *β-mer(N)*-$[Co(adao)CO_3]$ (1.4 g), of which preparative procedure was described in the previous paper,[1] was suspended in 3 cm^3 of iced cold water. To the suspension, 2 cm^3 of 6 M $HClO_4$ was added slowly drop by drop under cooling in an ice bath. The product was filtered out, and then the filtrate was evaporated below 40 °C with an aid of air stream. When the red crystals began to deposit, the reaction mixture was cooled sufficiently for the complete deposition. They were filtered, and washed with a mixture of ethanol and ether (1 : 2). Yield, ≈0.4 g.

Found: C, 15.24; H, 4.23; N, 8.97%. Calcd for $[Co(adao)(H_2O)_2](ClO_4)_2\cdot H_2O = CoC_6H_{20}N_3O_{13}Cl_2$: C, 15.27; H, 4.27; N, 8.90%.

Analyses. The carbon, hydrogen, and nitrogen in the isolated complexes were analyzed at the Microanalysis Center of Osaka University, and at the Analysis Center of the Institute for Chemical Reserch, Kyoto University.

Measurements. The absorption spectra in solution were measured with a Shimadzu UV-200 Recording Spectrophotometer using 1 cm or 10 cm silica cells. The diffuse reflectance spectra of solid samples in the range 340—750 nm were measured with a Hitachi EPU-2A Spectrophotometer equipped with a reflectance attachment (Type R-3), and MgO disks for the reference. The IR spectra were recorded with a JASCO IRA-1 Spectrophotometer by a Nujol mull method. The proton NMR spectra were recorded with a Varian XL-100 Spectrometer or a Japan Electron Optics JNM-4H-100 Spectrometer in a deuterium oxide, with *t*-butyl alcohol as the internal reference.

Results and Discussion

Preparative Remarks. The preparation routes for $[Co(adao)X_2]$ are shown schematically in Fig. 2. Schneider and Collman[3] reported that *β-mer(N)*-

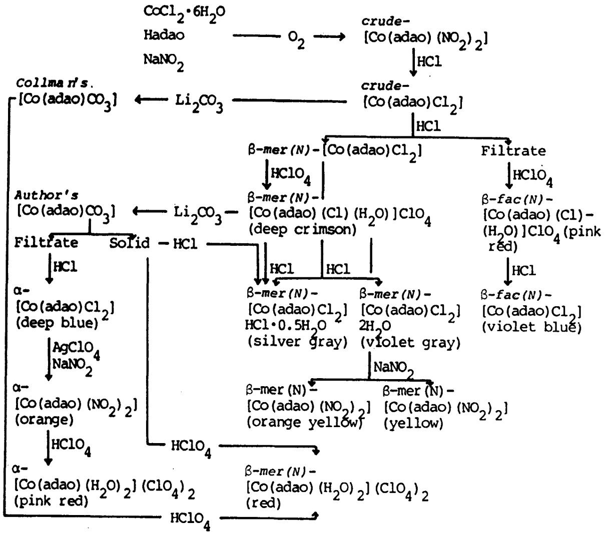

Fig. 2. The preparation scheme of $[Co(adao)X_2]$ (X= Cl^-, NO_2^-, and H_2O).

$[Co(adao)(NO_2)_2]$ could be obtained by air oxidation of the suspension of $CoCl_2 \cdot 6H_2O$, $NaNO_2$, and Hadao. However, the present author found that the *β-mer*(*N*)-dinitro isomer prepared according to the Collman's method *(1)* was different from the *β-mer*(*N*)-dinitro isomer which was prepared by the present author's method *(7)*, from the differences of their absorption spectra as well as their solubilities in water. It was also found that the reaction of the author's *β-mer*(*N*)-dinitro isomer and $HClO_4$ gave *β-mer*(*N*)-$[Co(adao)(NO_2)(H_2O)]ClO_4$ with a higher yield than that of the Collman's *β-mer*(*N*)-dinitro isomer and $HClO_4$. These facts indicate that the Collman's *β-mer*(*N*)-dinitro isomer contains another complex than *β-mer*(*N*)-$[Co(adao)(NO_2)_2]$. On the other hand, the author's method, in which the reaction of *β-mer*(*N*)-$[Co(adao)(Cl)(H_2O)]ClO_4$ and $NaNO_2$ was used, gave two kinds of *β-mer*(*N*)-$[Co(adao)(NO_2)_2]$ in a pure state *(7-a, b)*. α-, and *β-fac*(*N*)-$[Co(adao)(NO_2)_2]$ have not been isolated so far. For the isolation of these dinitro isomers, each reaction of α-$[Co(adao)(H_2O)_2]^{2+}$ or *β-fac*(*N*)-$[Co(adao)(Cl)(H_2O)]^+$ with sodium nitrite was attempted. Although the reaction of former complex afforded α-$[Co(adao)(NO_2)_2]$ *(6)*, the latter complex gave *β-fac*(*N*)-$[Co(adao)(Cl)(NO_2)]$ (this will be described elsewhere).

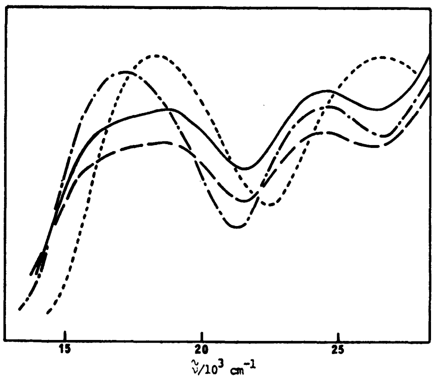

Fig. 3. The reflectance spectra of $[Co(adao)Cl_2]$.
—·—·—: α-$[Co(adao)Cl_2]$ (deep blue), ——: *β-mer* (*N*)-$[Co(adao)Cl_2] \cdot HCl \cdot 0.5H_2O$ (silver——gray), — —: *β-mer*(*N*)-$[Co(adao)Cl_2] \cdot 2H_2O$ (violet gray), ------: *β-fac*(*N*)-$[Co(adao)Cl_2]$ (violet blue).[a]
a) in HCl solution.

For the α-diaqua isomer, it was recognized that the aquation of α-$[Co(adao)Cl_2]$ with silver perchlorate in acidic solution gave the desired species. However, because of contamination with other salts such as silver chloride, it was difficult to isolate the α-diaqua isomer in a pure state. Hence, the preparation route using the α-dinitro isomer and $HClO_4$ was adopted for the isolation of α-$[Co(adao)(H_2O)_2](ClO_4)_2$ *(8)*.

The Structures of $[Co(adao)Cl_2]$ *Isomers.* As may be seen in Fig. 2, four kinds of isomers of $[Co(adao)Cl_2]$, deep blue, silver gray, violet gray, and violet blue isomers, could be isolated. Among these four dichloro isomers, the silver gray and violet gray isomers are sparingly soluble in HCl, while the yield of violet blue isomer is very poor. Therefore, three reflectance spectra of the deep blue, silver gray, and violet gray isomers are shown in Fig. 3, together with the absorption

TABLE 1. ELECTRONIC SPECTRAL DATA OF $[Co(adao)X_2]$

<table>
<tr><th rowspan="3">Complex</th><th rowspan="3">Color</th><th colspan="4">I</th><th colspan="2" rowspan="2">II or SP.[a]</th></tr>
<tr><th colspan="2">Ia</th><th colspan="2">Ib</th></tr>
<tr><th>$\frac{\tilde{\nu}_{max}}{cm^{-1}}$</th><th>$\left(\frac{\varepsilon}{mol^{-1}\,dm^3\,cm^{-1}}\right)$</th><th>$\frac{\tilde{\nu}_{max}}{cm^{-3}}$</th><th>$\left(\frac{\varepsilon}{mol^{-1}\,dm^3\,cm^{-1}}\right)$</th><th>$\frac{\tilde{\nu}_{max}}{cm^{-1}}$</th><th>$\left(\frac{\varepsilon}{mol^{-1}\,dm^3\,cm^{-1}}\right)$</th></tr>
<tr><td>α-$[Co(adao)Cl_2]$[b]</td><td>Deep blue</td><td colspan="4">17240</td><td>24670</td><td></td></tr>
<tr><td>*β-mer*(*N*)-
$[Co(adao)Cl_2] \cdot HCl$[b]</td><td>Silver gray</td><td>≈16100</td><td></td><td>18670</td><td></td><td>24500</td><td></td></tr>
<tr><td>*β-mer*(*N*)-
$[Co(adao)Cl_2] \cdot 2H_2O$[b]</td><td>Violet gray</td><td>≈16100</td><td></td><td>18670</td><td></td><td>24500</td><td></td></tr>
<tr><td>*β-fac*(*N*)-$[Co(adao)Cl_2]$</td><td>Violet blue</td><td colspan="4">18150 (194)</td><td>26230</td><td>(172)</td></tr>
<tr><td>α-$[Co(adao)(H_2O)_2](ClO_4)_2$</td><td>Pink red</td><td colspan="4">19450 (119)</td><td>27380</td><td>(98)</td></tr>
<tr><td>*β-mer*(*N*)-
$[Co(adao)(H_2O)_2](ClO_4)_2$</td><td>Red</td><td colspan="4">20340 (117)</td><td>27210</td><td>(112)</td></tr>
<tr><td>α-$[Co(adao)(NO_2)_2]$</td><td>Orange</td><td colspan="4">21820 (184)</td><td>30520</td><td>(4370)</td></tr>
<tr><td>*β-mer*(*N*)$[Co(adao)(NO_2)_2]$</td><td>Orange yellow</td><td colspan="4">22250 (255)</td><td>30860</td><td>(3800)</td></tr>
<tr><td>*β-mer*(*N*)$[Co(adao)(NO_2)_2]$</td><td>Yellow</td><td colspan="4">22370 (260)</td><td>31000</td><td>(3200)</td></tr>
</table>

a) Specific band due to the nitro ligand. b) Data of the reflectance spectra.

spectrum in solution for the violet blue isomer. Their electronic spectral data are summarized in Table 1. From Fig. 3, it is found that the first bands of silver gray and violet gray isomers show more pronounced splitting (≈16100, 18670 cm^{-1}) than that of the deep blue one (17240 cm^{-1}). Furthermore, it is found that the deep blue and violet blue isomers show symmetrical first absorption bands, although the first band of the violet blue isomer is observed at a higher wave number (18150 cm^{-1}) than that of the deep blue one (17480 cm^{-1}). Also in their second absorption bands, the band of violet blue isomer is located at a higher wave number (26230 cm^{-1}) than that of the deep blue one (25190 cm^{-1}).

In IR spectral measurements, all dichloro isomers show a strong band at around 1650 cm^{-1}. These spectral results suggest that their adao's carboxyl groups coordinate to the central cobalt.5,6) The IR spectral patterns assignable to the N–H stretching in the region of 3400—3100 cm^{-1} are not the same; these differences are proof for that the four dichloro isomers are different. It is further recognized that the violet blue isomer, which places the second absorption band at a higher wave number region, exhibits no peak due to the aqua ligand in any wave number region higher than 3400 cm^{-1}. This observation indicates that the violet blue isomer in the solid state is not an aquachloro complex.

Study of the ligating atoms of $[Co(adao)Cl_2]$ shows that the dichloro complex belongs to the complex of $[CoN_3OCl_2]$ type. In the case of *trans*(*Cl*)-$[CoCl_2(NH_3)_3(H_2O)]Cl$,7,8) its first band splits into two components (15870, 19470 cm^{-1}).9) When this splitting (3600 cm^{-1}) is compared with that of the silver gray $[Co(adao)Cl_2]$ (2570 cm^{-1}), the former is larger than the latter. Therefore, it is found that the silver gray isomer is not the *trans* one.

It was reported that the difference of the first d-d band splitting pattern in the Co(III) complexes mainly depends upon the symmetry of the complex.10,11) Then, Yamatera proposed the so-called "Yamatera's rule," which predicts the d-d bands splitting pattern in the Co(III) complex.12) It is possible to calculate the positions of the first band splitting components in the respective isomers of $[Co(adao)Cl_2]$ according to the Yamatera's rule.12) Their predicted positions are calculated by using the following three shift parameters: $\delta(N)=+330\ cm^{-1}$ (estimated from $[Co(en)_3]^{3+}$),13) $\delta(O)=-3800\ cm^{-1}$ (estimated from *fac*-$[Co(gly)_3]^{3+}$ and $[Co(en)_3]^{3+}$),13) and $\delta(Cl)=-10070\ cm^{-1}$ (estimated from *trans*(*Cl*)-$[CoCl_2(en)_2]^{+}$).14) This estimation indicates that the difference between the highest and the lowest wave number components increases in the order of $\alpha \simeq \beta$-*fac*(*N*)<β-*mer*(*N*)<*trans*.

From the comparison of this estimation and the observed absorption bands, it is found that the silver gray and violet gray isomers take the β-*mer*(*N*) coordination mode, and the deep blue and violet blue isomers, the α or β-*fac*(*N*) one. The reflectance spectral resemblance and IR spectral difference suggest that two kinds of β-*mer*(*N*)-dichloro isomers with the different *s*-N configurations were isolated. It is very difficult to decide their *s*-N configurations. However, Buckingham *et al.*15,16) obtained two diastereoisomers of β_1-$[Co(gly)(trien)]I_2$17) with the different *s*-N(trien) configurations. It was also found that Λ-β_1-$(S_N{}^aS_N{}^p)$-$[Co(gly)(trien)]I_2$18) is more stable than Λ-β_1-$(S_N{}^aR_N{}^p)$-$[Co(gly)(trien)]I_2$, on the basis of their isomerization experiments and strain energy calculations. Also in β_2-$[Co(gly)(trien)]Cl_2$,16,17) it was found that Λ-β_2-$(S_N{}^aS_N{}^p)$ isomer is more stable than the Λ-β_2-$(S_N{}^aR_N{}^p)$ one, and the former's yield is higher than the latter's. When these facts are considered, it is reasonable to assume that the *s*-N(adao) configurations of silver gray isomer with the higher yield are $(R_{N_1}^{a}S_{N_2}^{p}, S_{N_1}^{a}R_{N_2}^{p})$19) and those of violet gray with the lower yield are $(R_{N_1}^{a}R_{N_2}^{p}, S_{N_1}^{a}S_{N_2}^{p})$.

It is difficult to determine the structures of the deep blue and violet blue isomers on the basis of their reflectance spectra alone. In the case of the deep blue isomer, however, the absorption spectrum of the diaqua species, which was derived from the deep blue isomer by the treatment with $AgClO_4$ in acidic solution, resembles to that of α-$[Co(adao)(H_2O)_2](ClO_4)_2$, of which structure will be decided in the later section on the basis of the proton NMR spectrum. Furthermore, the reaction of α-$[Co(adao)(H_2O)_2](ClO_4)_2$ and HCl gave mainly the deep blue isomer. Therefore, the deep blue isomer seems to take the α structure. For the violet blue isomer, decisive data for the determination of its structure were not obtained. However, because the violet blue isomer was obtained from β-*fac*(*N*)-$[Co(adao)(Cl)(H_2O)]ClO_4$ by the treatment with HCl, and the deep blue isomer takes the α structure, the violet blue isomer is assigned to the β-*fac*(*N*) structure, at present.

The Structures of $[Co(adao)(NO_2)_2]$ *Isomers.* As is shown in Fig. 2, three isomers of $[Co(adao)(NO_2)_2]$, orange, orange yellow, and yellow isomers, were isolated. The orange isomer was derived from α-$[Co(adao)Cl_2]$ by the treatment with $NaNO_2$, and the orange yellow and yellow isomers were derived from β-*mer*(*N*)-$[Co(adao)(Cl)(H_2O)]ClO_4$. Differences in solubilities were observed among the three isomers, that is, at about 20 °C, 4230 cm^3 of H_2O was required for the dissolution

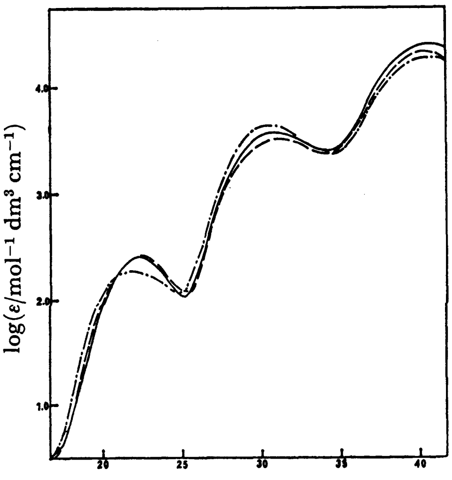

Fig. 4. The absorption spectra of $[Co(adao)(NO_2)_2]$. —·—·—: α-$[Co(adao)(NO_2)_2]$ (orange), ——: β-*mer*(*N*)-$[Co(adao)(NO_2)_2]$ (orange yellow), – – –: β-*mer*(*N*)-$[Co(adao)(NO_2)_2]$ (yellow).

of one gram orange isomer, 2500 cm^3 for the orange yellow, and 794 cm^3 for the yellow.

As is seen in Fig. 4, and Table 1, the first absorption band of orange yellow isomer is almost identical to that of the yellow one. On the other hand, the first band of orange isomer is broader than those of the other two isomers. It has been reported that the so-called nitro specific band of *trans* dinitrocobalt(III) complex is located at a lower wave number region (28570—29850 cm^{-1}) than that of the corresponding *cis* one.[10,14,20—26] Judging from the fact that the maxima of the nitro specific bands of three $[Co(adao)(NO_2)_2]$ are located at similar wave numbers (30520 cm^{-1} for the orange isomer, 30860 cm^{-1} for the orange yellow, and 31000 cm^{-1} for the yellow), the isomers are *cis*.

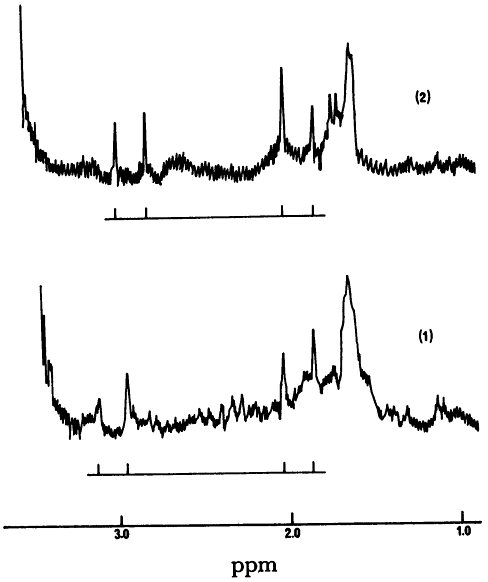

Fig. 5. The proton NMR spectra of $[Co(adao)(NO_2)_2]$.
(1): β-*mer*(*N*)-$[Co(adao)(NO_2)_2]$ (orange yellow), (2): β-*mer*(*N*)-$[Co(adao)(NO_2)_2]$ (yellow).

Although the proton NMR spectrum of orange isomer could not be measured because of its low solubility in D_2O, the proton NMR spectra of orange yellow and yellow isomers were obtained, as is shown in Fig. 5. The former's NMR spectrum shows one AB quartet in the range of 1.87 to 3.13 ppm, and the latter's one, in the range of 1.85 to 3.01 ppm. As can be inferred from the coordination modes of adao in Fig. 1-a, these four coordination modes may be classified into two groups from the standpoint of the disposition of adao glycinate ring.[27] One group is composed of the isomers with an apical glycinate ring (α and β-*mer*(*N*)), and another, those with an equatorial ring (β-*fac*(*N*) and *trans*). Therefore, the proton NMR spectra of the former should be different from those of the latter at the resonances of the glycinate ring protons.

It has been reported that a considerable difference exists between the proton NMR spectra for the isomers of $[Co(edda)(AA)]$ ($AA=(NH_3)_2$, en, ox, and mal),[28—31] that is, a AB quartet appears for the apical ring (R-ring)[32] protons and an apparent singlet for the equatorial ring (G-ring)[32] protons. It has also been observed in the proton NMR spectra of edda– and ed3a–Co(III) complexes that the value of $\delta_{AB}(=\delta_A-\delta_B)$[33] for the apical ring protons is in the range of 0.7 to 1.0 ppm, while that for the equatorial ring protons is in the range of 0.0 to 0.4 ppm.[29] The proton NMR spectra of two dinitro isomers (Fig. 5) show the AB quartet pattern, and their values of δ_{AB} are 1.09 ppm for the orange yellow isomer, and 0.96 ppm for the yellow one. Therefore, the orange yellow and yellow isomers take the α or β-*mer*(*N*) structure. Furthermore, it was found that the reaction of orange isomer and $HClO_4$ gave α-$[Co(adao)(H_2O)_2](ClO_4)_2$, as was described in Fig. 2. From these facts, it is inferred that the orange isomer takes the α structure.

When the same shift parameters as used in the previous case of $[Co(adao)Cl_2]$ and $\delta(NO_2)=+4300$ cm^{-1} (estimated from *mer*-$[Co(NO_2)_3(NH_3)_3]$ and *cis*-$[Co(NO_2)_2(NH_3)_4]^+$),[34,35] are used for the calculation of the first band components of four possible dinitro isomers, the Yamatera' srule suggests that the predicted first band of α isomer is broader than that of β-*mer*(*N*). Therefore, it is reasonable to assign the orange yellow and yellow isomers to the β-*mer*(*N*) structure, and the orange isomer, to the α one.

Consequently, it is certain that two kinds of β-*mer*(*N*) isomers were isolated also in $[Co(adao)(NO_2)_2]$. Furthermore, the difference of these β-*mer*(*N*) isomers is checked by the comparison of their IR spectra, which are shown in Fig. 6. For the assignment of their *s*-N configurations, it is inferred on the basis of their yields

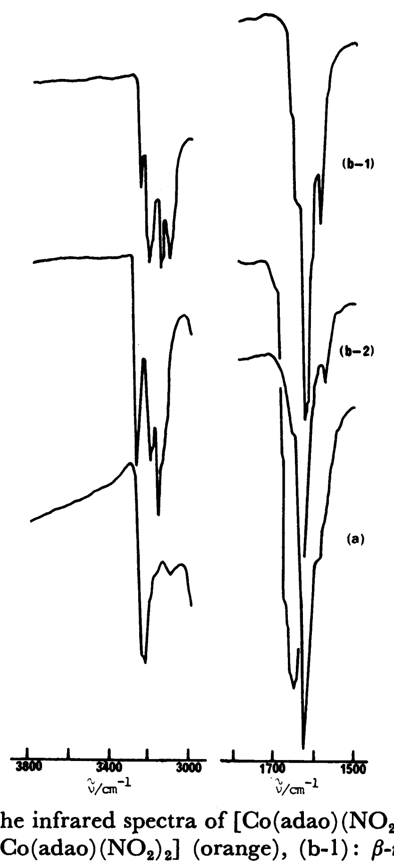

Fig. 6. The infrared spectra of $[Co(adao)(NO_2)_2]$.
(a): α-$[Co(adao)(NO_2)_2]$ (orange), (b-1): β-*mer*(*N*)-$[Co(adao)(NO_2)_2]$ (orange yellow), (b-2): β-*mer*(*N*)-$[Co(adao)(NO_2)_2]$ (yellow).

that the orange yellow isomers with a higher yield adopts the $(R_{N_1}^{a}S_{N_2}^{p}, S_{N_1}^{a}R_{N_2}^{p})$ configuration, and the yellow isomer with a lower yield, the $(R_{N_1}^{a}R_{N_2}^{p}, S_{N_1}^{a}S_{N_2}^{p})$ one.

The Structures of $[Co(adao)(H_2O)_2](ClO_4)_2$ *Isomers.* Four possible geometrical isomers of the diaqua complex belonging to a type of $[CoN_3O_3]$ may be classified into two groups, that is, the α and *β-fac*(*N*) isomers belong to a *fac*-$[CoN_3O_3]$ type, and the *β-mer*(*N*) and *trans* isomers, to a *mer*-one. It is well known that the first band of the *mer*-type is broader than that of the *fac*-one.[36–39] In Fig. 7, the absorption spectra of the pink red and red isomers are shown, and in Table 1, their numerical data are summarized.

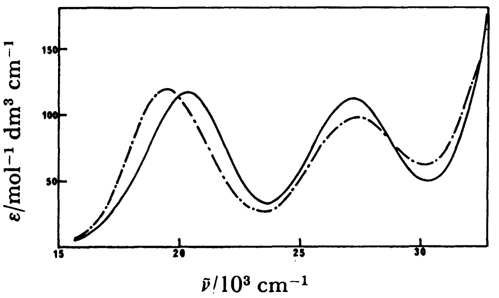

Fig. 7. The absorption spectra of $[Co(adao)(H_2O)_2](ClO_4)_2$.
–·–·–: α-$[Co(adao)(H_2O)_2](ClO_4)_2$ (pink red), ——: *β-mer*(*N*)-$[Co(adao)(H_2O)_2](ClO_4)_2$ (red).

As is seen in Fig. 7, the half width of first absorption band for the pink red isomer is almost identical to that for the red one. On account of this, their structures can not be distinguished by the application of the empirical rule for the first band width in a $[CoN_3O_3]$ complex.[36–39] However, the first absorption maximum of the red isomer is located at a higher wave number than that of the pink red one. On the contrary, the second band maximum of the former is located at a lower wave number than that of the latter.

It has been found that the first band of *mer*-$[Co(NH_3)_3(H_2O)_3]^{3+}$ is broader than that of the *fac*-one, and that the apparent first band maximum of the *mer* isomer is located at a higher wave number than that of the *fac* one.[40,41] Furthermore, it has been reported that *mer*-$[Co(dien)(H_2O)_3]^{3+}$ places the first band maximum at a higher wave number than that of the corresponding *fac* one, although these isomers have not been obtained as crystalline forms.[42,43] On the basis of the different first band positions, it is found that the red isomer adopts the *β-mer*(*N*) or the *trans* structure, and the pink red one, the α or the *β-fac*(*N*) structure.

The proton NMR spectrum shows one AB quartet pattern in the range of 2.16 to 3.20 ppm for the red isomer, and in the range of 2.15 to 3.13 ppm for the pink red one. These observations suggest that the coordination mode of adao in each isolated isomer is either the α or the *β-mer*(*N*) one. Taking into consideration of their preparative routes (Fig. 2), it can be concluded that the red isomer is the *β-mer*(*N*) one, and the pink red, the α.

Summary. In the three kinds of $[Co(adao)X_2]$ type complexes ($X=Cl^-$, NO_2^-, and H_2O), α and *β-mer*(*N*) isomers were isolated. Consequently, the previously unknown α coordination mode could be established also in $[Co(adao)X_2]$ type complex. As to the *cis*(*Cl*)-$[CoN_3OCl_2]$ type complex, the *β-fac*(*N*)-$[Co(adao)Cl_2]$ besides the α- and *β-mer*(*N*)-$[Co(adao)Cl_2]$ were also detected. Furthermore, two kinds of *β-mer*(*N*) isomers could be isolated in the cases of $[Co(adao)Cl_2]$ and $[Co(adao)(NO_2)_2]$. From the comparison of the yields in a pair of *β-mer*(*N*) isomers respectively, it is inferred that the silver gray dichloro and the orange yellow dinitro complexes, which were isolated with the higher yields, adopt the $(R_{N_1}^{a}S_{N_2}^{p}, S_{N_1}^{a}R_{N_2}^{p})$ configurations, while the violet gray dichloro and yellow dinitro complexes, which were isolated with the lower yields, adopt the $(R_{N_1}^{a}R_{N_2}^{p}, S_{N_1}^{a}S_{N_2}^{p})$ configurations.

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17) The prefix β_1 refers to the isomer with the nitrogen atom of glycinate ligand *trans* to the primary amine of trien.

The prefix β_2 refers to the isomer with the nitrogen atom of glycinate ligand *trans* to the *s*-N^p(trien).[18]

18) The two kinds of *s*-N(trien) dispositions are discriminated by using the superscripts of a (angular) and p (planar): N^a or N^p.

19) The two kinds of *s*-N(adao) are discriminated by numbering as follows: O–N_1–N_2–N. Furthermore, the two *s*-N(adao) dispositions, angular and planar, are represented with the same notation as used for the *s*-N(trien) ones.[18]

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