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Studies of the Cobalt(III) Complexes of 8-Amino-3,6-diazaoctanate Ion. IV.[1] Preparations and Some Properties of [Co(ADAO)XY] Type Complexes: XY=Cl(NH$_3$), Cl(py), (H$_2$O)(py), Cl(H$_2$O), (NO$_2$)(H$_2$O), and Cl(NO$_2$)

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The following new cobalt(III) complexes containing the 8-amino-3,6-diazaoctanate ion (adao[2]) have been isolated: two isomers of *β-mer*(*N*)-*trans*(*Cl*,O_{adao})-[Co(adao)(Cl)(NH$_3$)]ClO$_4$, two isomers of *β-mer*(*N*)-*trans*(*Cl*, O_{adao})-[Co(adao)(Cl)(py)]ClO$_4$, *β-mer*(*N*)-*trans*(*O*)-[Co(adao)(H$_2$O)(py)]ClO$_4$·bcs,[2] *β-mer*(*N*)-*trans*(*Cl*,O_{adao})-[Co(adao)(Cl)(H$_2$O)]ClO$_4$, *β-fac*(*N*)-[Co(adao)(Cl)(H$_2$O)]ClO$_4$, *β-mer*(*N*)-*cis*(*O*)-[Co(adao)(NO$_2$)(H$_2$O)]ClO$_4$, and *β-fac*(*N*)-[Co(adao)(Cl)(NO$_2$)]. The geometrical structures have been determined on the basis of the absorption spectra, the proton NMR spectra, and the consideration of their preparative processes.

In the case of [Co(adao)XY] type complex, in which two different unidentate ligands (X and Y) occupy the residual two coordination sites, seven geometrical isomers, two α, two *β-mer*(*N*), two *β-fac*(*N*), and *trans*,[3] are possible, as shown in Fig. 1. The isolation of [Co(adao)XY] type complex has not been performed so far. It is necessary to isolate the complexes of [Co(adao)XY] type for the establishment of the stereochemistry of adao-Co(III) complex. In a previous paper,[1] it was reported that the deep crimson [Co(adao)(Cl)(H$_2$O)]ClO$_4$ was used as the starting material for the preparation of [Co(adao)X$_2$] type complexes. However, the structure of the deep crimson aquachloro isomer could not be decided yet. For its structural determination, it is essential to isolate many various kinds of [Co(adao)XY] isomers as well as the other aquachloro isomers.

In addition, two kinds of *β-mer*(*N*) racemic isomers with different configurations of the adao's secondary amine (*s*-N) were isolated in some complexes of [Co(adao)X$_2$] type (X=NO$_2^-$ and Cl$^-$), as was described in the previous paper.[1] When the configurations of *s*-N in [Co(adao)XY] type complexes are considered, twelve kinds of racemic isomers are possible: namely, two α, four *β-mer*(*N*), *four β-fac*(*N*), and two *trans* ones. As an example, the *s*-N configurations of Λ-*β-mer*(*N*)-[Co(adao)XY] are shown in Fig. 2. Thus, the following four *β-mer*(*N*) racemic isomers are able to exist: *trans*(X,O_{adao})-($R_{\mathrm{N}_1^{\mathrm{a}}}S_{\mathrm{N}_2^{\mathrm{p}}}$,$S_{\mathrm{N}_1^{\mathrm{a}}}R_{\mathrm{N}_2^{\mathrm{p}}}$), *trans*($X$,$O_{\mathrm{adao}}$)-($R_{\mathrm{N}_1^{\mathrm{a}}}R_{\mathrm{N}_2^{\mathrm{p}}}$,$S_{\mathrm{N}_1^{\mathrm{a}}}S_{\mathrm{N}_2^{\mathrm{p}}}$), *cis*($X$,$O_{\mathrm{adao}}$)-($R_{\mathrm{N}_1^{\mathrm{a}}}S_{\mathrm{N}_2^{\mathrm{p}}}$,$S_{\mathrm{N}_1^{\mathrm{a}}}S_{\mathrm{N}_2^{\mathrm{p}}}$), *cis*($X$,$O_{\mathrm{adao}}$)-($R_{\mathrm{N}_1^{\mathrm{a}}}R_{\mathrm{N}_2^{\mathrm{p}}}$,$S_{\mathrm{N}_1^{\mathrm{a}}}S_{\mathrm{N}_2^{\mathrm{p}}}$).[4–6] Therefore, the isolations of isomers with the different *s*-N configurations are attempted also in [Co(adao)XY] type complex.

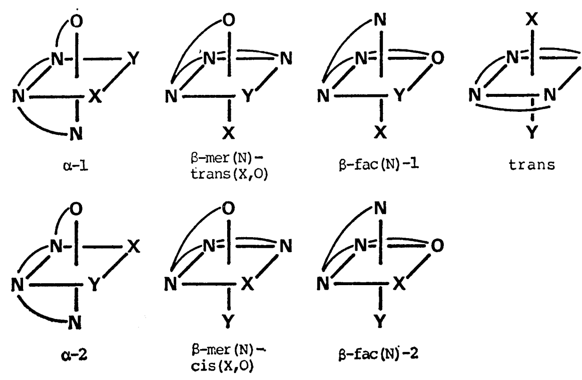

Fig. 1. The possible geometrical isomers of [Co(adao)-XY] type complex.

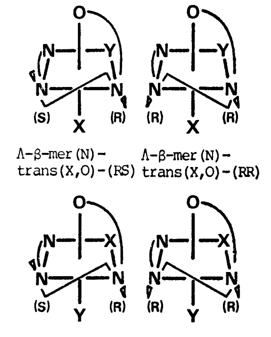

Fig. 2. The possible isomers of Λ-*β-mer*(*N*)-[Co(adao)-XY] under consideration of *s*-N configurations.

Experimental

Preparations of Complexes. *(1) β*-mer(N)-*[Co(adao)(Cl)(H$_2$O)]ClO$_4$*: The crude [Co(adao)Cl$_2$] (50 g)[1] was suspended in 400 cm^3 of 1 M (1 M=1 mol dm^{-3}) HClO$_4$, and the suspension was heated at about 65 °C in a water bath. The gray starting materials began to dissolve, at the same time the deep crimson crystals appeared. After the reaction mixture was allowed to stand at 65 °C for 20 min, it was cooled in an ice bath, and then filtered. The crystals were washed with a mixture of ethanol and ether (1:1). Upon recrystallization from 0.1 M HClO$_4$, *β-mer*(*N*)-[Co(adao)-Cl)(H$_2$O)]ClO$_4$ precipitated as deep crimson crystals. Yield, 40 g.

Found: C, 19.32; H, 4.35; N, 11.28%. Calcd for [Co(adao)(Cl)(H$_2$O)]ClO$_4$=CoC$_6$H$_{16}$N$_3$O$_7$Cl$_2$: C, 19,37; H, 4.33; N, 11.29%.

(2) β-fac(N)-*[Co(adao)(Cl)(H$_2$O)]ClO$_4$*: Method A, from the crude *β-fac*(*N*)-[Co(adao)Cl$_2$]; The reserved filtrate, which was obtained in the preparation of the crude [Co(adao)Cl$_2$] as described in the previous paper,[1] was concentrated on a water bath with the aid of an air stream, whereupon the brown material appeared. After the product was cooled, the brown material was filtered off. The procedures of concentration and removal were repeated two or three times. When the last deep blue filtrate obtained was further evaporated with the same method mentioned

above, tarry material was obtained. To this tarry material, ethanol (≈100 cm^3) was added. When the mixture was stirred with a glass rod, the spherical oily material was sedimented. The blue supernatant solution was decanted. When the oily material was washed two times with 50 cm^3 portions of ethanol by decantation, it changed to a crystalline material. These crystals were collected on a filter, and then washed with ethanol. Yield, 3 g. Although recrystallization was repeated, it was found that the blue crystals were not composed of pure *β-fac*(*N*)-dichloro isomer. This blue crystal will be named as the "crude *β-fac*(*N*)-[Co(adao)Cl_2]" in the subsequent part.

The crude *β-fac*(*N*)-[Co(adao)Cl_2] (3 g) was suspended in 10 cm^3 of water, and then 5 cm^3 of 2 M $HClO_4$ was added to the suspension. The mixture was concentrated on a water bath with the aid of an air stream. Furthermore, 10 cm^3 of water and 5 cm^3 of 2 M $HClO_4$ were added to this concentrated product, and then the mixture was concentrated by the method mentioned above. When the treatment was repeated two or three times, pink red crystals began to appear. These crystals were dissolved in about 10 cm^3 of water, and the solution was filtered once. The filtrate was concentrated by the same method until the crystals appeared. The pink red crystals were separated by filtration, and then washed with ethanol and ether. Yield, 0.15 g.

Found: C, 18.46; H, 4.49; N, 10.83%. Calcd for [Co(adao)(Cl)(H_2O)]$ClO_4 \cdot H_2O$ = $CoC_6H_{18}N_3O_8Cl_2$: C, 18.48; H, 4.65; N, 10.77%.

Method B, from *β-fac*(*N*)-[Co(adao)(Cl)(NO_2)]; To the suspension of *β-fac*(*N*)-[Co(adao)(Cl)(NO_2)] (0.3 g) in 5 cm^3 of water (whose preparative method will be described in the following procedure (*6*)) was added 1 cm^3 of 1 M $HClO_4$ drop by drop. The suspension was concentrated to dryness on a water bath under an air stream. After the product was allowed to stand at room temperature for some time, 5 cm^3 of water and 2 cm^3 of 1 M $HClO_4$ were added to the product, and then the mixture was concentrated to dryness again. This treatment was repeated once more to force the aquation of the starting material to completion. The product was dissolved in 10 cm^3 of water, and then filtered. The filtrate was evaporated until pink red crystals began to deposit out. After cooling, the crystals were collected on a filter, and then washed with ethanol and ether. Yield, 0.25 g. The identity of this crystal and the pink red isomer obtained in the Method A was checked by the absorption spectra.

Method C, the chromatographic separation of the product obtained from the crude *β-fac*(*N*)-[Co(adao)Cl_2]; The crude *β-fac*(*N*)-[Co(adao)Cl_2] (3 g) was suspended in 10 cm^3 of water, and then 5 cm^3 of 2 M $HClO_4$ was added. The mixture was treated with the method described in the Method A. After the violet precipitate obtained was removed by filtration, the filtrate was diluted with 10 cm^3 of water. To the diluted solution was added ethanol, whereupon pink red crystals were deposited. After the removal of these crystals by filtration, the filtrate obtained was poured into a column (ϕ 50 mm × l 400 mm) containing a gel ion-exchange (SP-Sephadex C-25, Na^+ form). The column was swept with water, and then the adsorbed band at top of the column was eluted with an aqueous sodium perchlorate solution. By elution with 0.01—0.06 M $NaClO_4$, the adsorbed band was progressively separated into six bands, which were deep crimson (I), pink red (II), red (III), violet red (IV), red (V), and red (VI), in the order of elution. From their absorption spectra, it was found that these eluates contained the following isomers. Of the earlier two eluates, (I) consisted of *β-mer(N)*-[Co(adao)(Cl)(H_2O)]$^+$, and (II), *β-fac(N)*-[Co(adao)(Cl)(H_2O)]$^+$. In the case of the middle two eluates, it was certain that (III) was composed of *β-mer*(*N*)-[Co(adao)$(H_2O)_2$]$^{2+}$, although the structure of the isomer contained in (IV) could not be determined. Each of the latter two eluates ((V) and (VI)) consisted of an isomer with the dimeric structure. For the isolation of *β-fac*(*N*)-[Co(adao)(Cl)(H_2O)]ClO_4, (II) (≈3 dm^3), which was eluted with 0.01 M $NaClO_4$, was concentrated to about 5 cm^3 in a rotary evaporator below 40 °C. This concentrated solution was allowed to stand overnight in a refrigerator, whereupon the pink red needles were precipitated. After filtration, these were washed with ethanol, and then with ether. Yield, 0.1 g.

It was found that the visible absorption spectrum of the isolated isomer is identical to that of the pink red one in Method A or B.

(3) *β*-mer(N)-trans(Cl,O_{adao})-[*Co(adao)(Cl)(NH_3)*]*ClO_4*: To the suspension of *β-mer*(*N*)-[Co(adao)(Cl)(H_2O)]ClO_4 (3.8 g) in 20 cm^3 of water was added 2 cm^3 of 14% ammonia, and then the mixture was heated at 75 °C for 3 h with stirring. After cooling, deposited crystals were filtered off. The filtrate was evaporated at 50 °C with the aid of an air stream until the pale brown crystals began to appear. The product was cooled and filtered. The crystals collected on a filter were washed with ethanol and ether. Yield, 0.5 g. The filtrate which was obtained in this stage was reserved for the isolation of another isomer.

Recrystallization of the pale brown crystals was carried out by the method of fractional extraction with hot (≈75 °C) 0.1 M $HClO_4$ as follows. The first and the second extracts were cooled in an ice bath, whereupon the pale brown crystals with enough purity deposited out. They were washed with ethanol and ether. The total yield was about 0.3 g.

When the reserved filtrate (≈5 cm^3) was further evaporated, reddish brown crystals deposited out. After cooling, they were collected on a filter, and then washed with ethanol. Yield, 1.5 g. They were recrystallized by a method similar to that described above. The total yield was about 0.2 g.

Found: C, 19.35; H, 4.70; N, 15.45% for the pale brown isomer; C, 19.10; H, 4.70; N, 15.57% for the reddish brown one. Calcd for [Co(adao)(Cl)(NH_3)]ClO_4 = $CoC_6H_{17}N_4O_6Cl_2$: C, 19.42; H, 4.62; N, 15.10%.

The reaction in the presence of active charcoal was also carried out. However, only one reddish brown isomer could be isolated together with *β-mer*(*N*)-[Co(adao)$(NH_3)_2$]$(ClO_4)_2$.[7]

(4) *β*-mer(N)-trans(Cl,O_{adao})-[*Co(adao)(Cl)(py)*]*ClO_4*: To the suspension of *β-mer*(*N*)-[Co(adao)(Cl)(H_2O)]ClO_4 (1.9 g) in 10 cm^3 of water was added 1 cm^3 of pyridine, and then the mixture was stirred at ≈80 °C for 2 h. After that, the product was cooled in an ice bath, whereupon reddish brown needles precipitated. The crystals were separated by filtration, and then washed with ethanol. The yield of first precipitate was about 0.9 g.

When the filtrate was concentrated furthermore at 40 °C, massive crystals with a dull reddish brown color began to deposit out. After cooling, they were filtered and washed with ethanol. The yield of second precipitate was about 0.4 g.

Recrystallization was carried out by the fractional extraction as follows; the first precipitate was extracted with three 3 cm^3 portions of hot (≈75 °C) 0.1 M $HClO_4$. Of these three extracts, the first and second extracts gave the pure reddish brown needles. The total yield was about 0.15 g. The second precipitate was extracted with five 2 cm^3 portions of hot 0.1 M $HClO_4$. All these extracts gave pure dull reddish brown massive crystals. The total yield was about 0.3 g.

Found: C, 30.33; H, 4.71; N, 13.39% for the reddish brown isomer; C, 30.09; H, 4.65; N, 13.40% for the dull reddish brown one. Calcd for [Co(adao)(Cl)(py)]ClO_4=$CoC_{11}H_{19}N_4O_6Cl_2$: C, 30.50; H, 4.42; N, 12.94%.

*(5) β-*mer(N)-trans(O)-*[Co(adao)(H_2O)(py)]ClO_4·bcs·2H_2O:*[2)] The author's carbonato complex (3 g)[8)] was suspended in 15 cm^3 of water. After 3.5 cm^3 of 6 M $HClO_4$ was added to the suspension, pyridine (3.5 cm^3) and active charcoal (0.5 g) were added in this order. The mixture was heated at 55 °C for 7 h with mechanical stirring. After the charcoal was separated on a filter, it was washed with two 10 cm^3 portions of hot water (≈80 °C). The washings and filtrate were combined, and the combined solution was evaporated to about 25 cm^3 at 55 °C in an air stream. After cooling, the first precipitate was filtered off. The filtrate was evaporated again, and then the second precipitate was also removed. On further concentrating, the third precipitate began to appear. After cooling, the precipitate was collected on a filter, and then washed with an ethanol–ether mixture (1:1). Yield, 0.7 g.

The above procedure was repeated three times to get enough crude *trans*(*O*)-aquapyridine complex deposited as the third precipitate. This crude complex (≈2 g) was dissolved in 20 cm^3 of water, and then 10 cm^3 of solution containing NH_4bcs (1.3 g)[2)] was added to it. After the mixture was heated at 55 °C for 5 min, it was allowed to stand for about 6 h at room temperature. Brown orange crystals deposited out. They were collected on a filter, and then washed with a ethanol–ether (1:1) and with ether. Yield, 0.18 g. The filtrate was kept overnight in a refrigerator, whereupon the same crystals were obtained. Yield, 0.36 g.

Upon recrystallization from 3 cm^3 of hot water (≈70 °C) containing the crude diastereoisomer (0.25 g), the pure brown orange crystals were precipitated. Yield, 0.1 g.

Found: C, 33.12; H, 5.18; N, 7.40%. Calcd for [Co(adao)(H_2O)(py)] ClO_4·bcs·2H_2O = $CoC_{21}H_{39}N_4O_{13}ClBrS$: C, 33.11; H, 5.16; N, 7.35%.

*(6) β-*fac(N)-*[Co(adao)(Cl)(NO_2)]*: To the solution of *β-fac*(*N*)-[Co(adao)(Cl)(H_2O)]ClO_4·H_2O (0.1 g) dissolved in 20 cm^3 of water was added $NaNO_2$ (0.1 g), and then the mixture was heated at 75 °C for 15 min, whereupon orange crystals began to deposit gradually. After the heating was continued for 10 min more to achieve the complete reaction, the product was cooled. The crystals precipitated were separated by filtration, and then washed with ethanol and with ether. Yield, 0.05 g.

Found: C, 24.25; H, 4.44; N, 18.92%. Calcd for [Co(adao)(Cl)(NO_2)]=$CoC_6H_{14}N_4O_4Cl$: C, 23.98; H, 4.70; N, 18.64%.

*(7) β-*mer(N)-cis(O)-*[Co(adao)(NO_2)(H_2O)]ClO_4*: The sparingly soluble *β-mer*(*N*)-[Co(adao)$(NO_2)_2$] (1.3 g), of which preparative procedure was reported in the previous paper,[1)] was covered with 5 cm^3 of 2 M $HClO_4$, and then the mixture was heated at about 80 °C on a water bath. When the mixture was heated for 5 min, the starting material began to dissolve, and soon orange crystals began to appear. It was heated for 15 min more to complete the reaction, and then cooled. The crystals were filtered, then washed with ethanol and with ether. Yield, 1.1 g.

They were recrystallized from 5 cm^3 of hot water (≈80 °C) by fractional extraction. The first and second extracts gave the pure crystals. The total yield was 0.6 g.

Although the reaction of Collman's dinitro complex[3)] and $HClO_4$ afforded also the same isomer, the yield is lower than that in the reaction using this sparingly soluble *β-mer*(*N*)-dinitro isomer[1)] as the starting material.

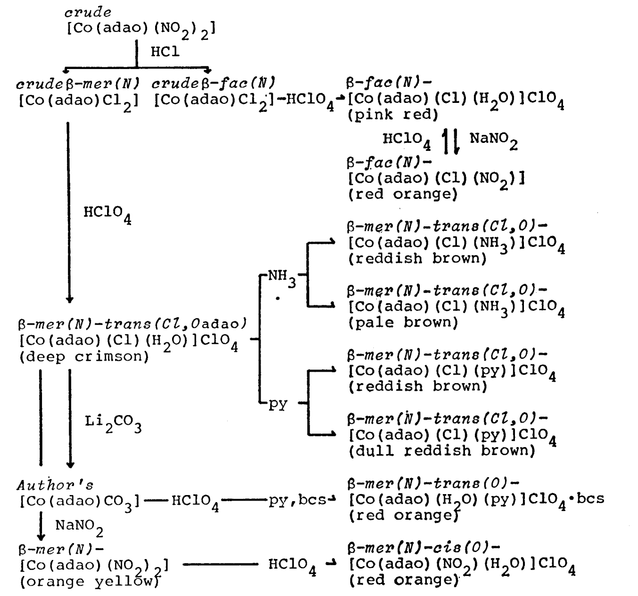

Fig. 3. The preparation scheme of [Co(adao)XY].

Found: C, 18.42; H, 4.47; N, 14.55%. Calcd for [Co(adao)(NO_2)(H_2O)]ClO_4=$CoC_6H_{16}N_4O_9Cl$: C, 18.84; H, 4.22; N, 14.64%.

Analyses. The carbon, hydrogen, and nitrogen in the isolated complexes were analyzed at the Microanalysis Center of Osaka University.

Measurements. The visible and ultraviolet absorption spectra were measured with a Shimadzu UV-200 Recording Spectrophotometer using 1 cm or 10 cm silica cells. 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 JEOL JNM-4H-100 Spectrometer in deuterium oxide, with *t*-butyl alcohol as the internal reference.

Results and Discussion

Preparative Remarks. As seen in Fig. 3, which shows the preparative scheme of [Co(adao)XY], the two aquachloro isomers with an deep crimson color or a pink red one were mainly used as the starting materials. The deep crimson isomer was isolated from crude *β-mer*(*N*)-[Co(adao)Cl_2] by the treatment with 1 M $HClO_4$ (*1*), and the pink red one was precipitated from the last blue filtrate containing the crude *β-fac*(*N*)-dichloro isomer (Method A in *2*) or the *β-fac*(*N*)-[Co(adao)(Cl)(NO_2)] (Method B in *2*) by using 6 M $HClO_4$ as the selective precipitant or reactant. Similar substitution reactions to that of the crude *β-mer*(*N*)-[Co(adao)Cl_2] and 1 M $HClO_4$ were observed in the synthesizing reactions of *β-mer*(*N*)-*trans*(*O*)-[Co(adao)-(H_2O)(py)]ClO_4·bcs (*5*) and *β-mer*(*N*)-*cis*(*O*)-[Co(adao)(NO_2)(H_2O)]ClO_4 (*7*). These facts suggest that in the substitution reaction of *β-mer*(*N*) isomer, the dissociation rates for the two unidentate ligands which are situated in the different coordination sites are different: that is, the unidentate ligand occupying the *cis* site to the "O_{adao}" is more dissociative than the other unidentate ligand occupying the *trans* site.

Table 1. Electronic spectral data of [Co(adao)XY]

Complex	Color	Ia	Ib	II
		$\frac{\tilde{\nu}_{max}}{cm^{-1}}\left(\frac{\varepsilon}{mol^{-1}\,dm^3\,cm^{-1}}\right)$	$\frac{\tilde{\nu}_{max}}{cm^{-1}}\left(\frac{\varepsilon}{mol^{-1}\,dm^3\,cm^{-1}}\right)$	$\frac{\tilde{\nu}_{max}}{cm^{-1}}\left(\frac{\varepsilon}{mol^{-1}\,dm^3\,cm^{-1}}\right)$
β-mer(N)-trans(Cl,O)-[Co(adao)(Cl)(NH$_3$)]ClO$_4$[a)]	Reddish brown	17500(66)	21730(69)	27340(125)
β-mer(N)-trans(Cl,O)-[Co(adao)(Cl)(NH$_3$)]ClO$_4$[a)]	Pale brown	17540(56)	21670(84)	sh.
β-mer(N)-trans(Cl,O)-[Co(adao)(Cl)(py)]ClO$_4$[a)]	Reddish brown	17580(65)	21550(83)	26880(132)
β-mer(N)-trans(Cl,O)-[Co(adao)(Cl)(py)]ClO$_4$[a)]	Dull reddish brown	17570(59)	21510(89)	sh.
β-mer(N)-trans(O)-[Co(adao)(H$_2$O)(py)]ClO$_4$·bcs	Brown orange	≈18900	21790(98)	28140(110)
β-mer(N)-trans(Cl,O$_{adao}$)-[Co(adao)(Cl)(H$_2$O)]ClO$_4$[b)]	Deep crimson	≈17200	19830(94)	25830(132)
β-fac(N)-[Co(adao)(Cl)(H$_2$O)]ClO$_4$[a)]	Pink red	19140(137)		27030(149)
β-mer(N)-cis(O)-[Co(adao)(NO$_2$)(H$_2$O)]ClO$_4$	Red orange	20750(182)		29760(1652)[c)]
β-fac(N)-[Co(adao)(Cl)(NO$_2$)]	Red orange	20830(180)		30490(2000)[c)]

a) Measured in 0.1 M HClO$_4$. b) Measured in 0.1 M HCl. c) Nitro specific band.

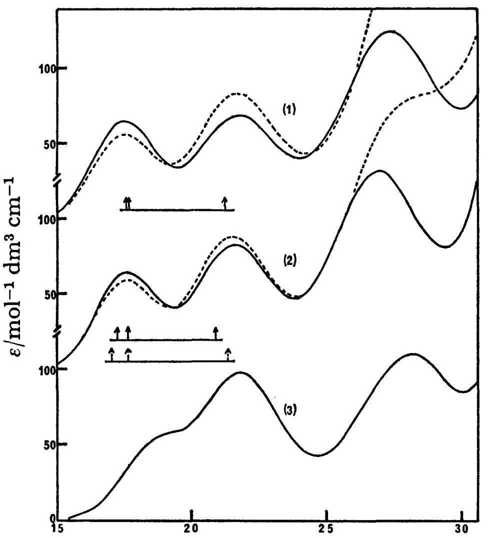

Fig. 4. The absorption spectra of [Co(adao)XY] type complexes and the predicted first band components.
(1): *β-mer(N)-trans(Cl,O$_{adao}$)*-[Co(adao)(Cl)(NH$_3$)]-ClO$_4$.
——: Reddish brown, - - -: pale brown. a) $\delta(N)=+330$ cm^{-1}, $\delta(O)=-3800$ cm^{-1}, and $\delta(Cl)=-10070$ cm^{-1} are used in the case of solid arrows.
(2): *β-mer(N)-trans(Cl,O$_{adao}$)*-[Co(adao)(Cl)(py)]ClO$_4$.
——: Reddish brown, - - -: dull reddish brown. b) $\delta(N)=+330$ cm^{-1}, $\delta(O)=-3800$ cm^{-1} are used in the case of solid arrows, and $\delta(N_{adao})=+970$ cm^{-1}, $\delta(O_{adao})=-5190$ cm^{-1}, in the case of dotted arrows.
(3): *β-mer(N)-trans(O)*-[Co(adao)(H$_2$O)(py)]ClO$_4$·bcs.
——: Brown orange.

Furthermore, it was recognized that under only the mild reaction conditions, pairs of isomers with the different *s*-N configuration can be isolated in *β-mer(N)-trans(Cl,O$_{adao}$)*-[Co(adao)(Cl)(NH$_3$)]ClO$_4$ and *β-mer(N)-trans(Cl,O$_{adao}$)*-[Co(adao)(Cl)(py)]ClO$_4$, respectively.

The Structures of [Co(adao)(Cl)(NH$_3$)]ClO$_4$. As mentioned in procedure (*3*), the reddish brown and pale brown isomers were isolated. Their elemental analyses corresponded well to the composition of [Co(adao)(Cl)(NH$_3$)]ClO$_4$. Although there are small differences between their absorption spectra, which are shown in Fig. 4, the spectra show a similar pattern in the region of their first absorption bands. Namely, the positions of two split components are located at 17500 cm^{-1} and 21730 cm^{-1} for the reddish brown isomer, and at 17540 cm^{-1} and 21670 cm^{-1} for the pale brown one (Table 1).

When the following shift parameters, $\delta(N)=+330$ cm^{-1},[9)] $\delta(O)=-3800$ cm^{-1},[9)] $\delta(Cl)=-10070$ cm^{-1},[10)] and $\delta(NH_3)=0$,[9)] which were used in the previous paper,[1)] are used, the first band components of *β-mer(N)-trans(Cl,O$_{adao}$)*-[Co(adao)(Cl)(NH$_3$)]$^+$ can be predicted as is shown with the solid arrows in Fig. 4. These predicted components fit approximately to the observed first band maxima. Therefore, the reddish brown and pale brown isomers can be assigned to the *β-mer(N)-trans(Cl,O$_{adao}$)* structure.

However, it is recognized from Fig. 4 that the observed higher wave number components (21730 cm^{-1} for the reddish brown and 21670 cm^{-1} for the pale brown) are located at the higher wave number than the predicted highest one (21220 cm^{-1}). These discrepancies suggest that the practical $\delta(N_{adao})$ in [Co(adao)(Cl)(NH$_3$)]ClO$_4$ is larger than $\delta(N)=+330$ cm^{-1} which was used in the above calculation. In order to estimate new adao shift parameter values ($\delta(N_{adao})$ and $\delta(O_{adao})$), the following calculations are made by using the mean value of the corresponding observed split band's positions for two kinds of *β-mer(N)-trans(Cl,O$_{adao}$)*-[Co(adao)(Cl)(NH$_3$)]ClO$_4$. In the higher wave number component, the following equation is written:

$$3/4\,\delta(N_{\text{adao}}) + 1/4\,\delta(NH_3) = 21700 - 20970 = +730\ (\text{cm}^{-1}) \qquad (1)$$

When it is assumed that the lower wave number maximum is observed as the mean of two lower wave number component positions, the following equation also holds.

$$\begin{aligned}&1/2[\{2/4\,\delta(N_{\text{adao}}) + 1/4\,\delta(O_{\text{adao}}) + 1/4\,\delta(Cl)\}\\ &+\{1/4\,\delta(N_{\text{adao}}) + 1/4\,\delta(NH_3) + 1/4\,\delta(O_{\text{adao}}) + 1/4\,\delta(Cl)\}]\\ &= 3/8\,\delta(N_{\text{adao}}) + 1/8\,\delta(NH_3) + 1/4\,\delta(O_{\text{adao}}) + 1/4\,\delta(Cl)\\ &= 17520 - 20970 = -3450\ (\text{cm}^{-1}) \qquad (2)\end{aligned}$$

Because $\delta(NH_3)=0$,[9] the value of $\delta(N_{\text{adao}})$ is obtained as $+970\ \text{cm}^{-1}$ from Eq. 1. Substituting this value into Eq. 2, the value of $\delta(O_{\text{adao}})$ is also obtained as $-5190\ \text{cm}^{-1}$. Here, the value of $\delta(Cl)=-10070\ \text{cm}^{-1}$ [10] is used.

The Structures of $[Co(adao)(Cl)(py)]ClO_4$. In the case of $[\text{Co(adao)(Cl)(py)}]\text{ClO}_4$, two isomers with a reddish brown color and dull reddish brown one were isolated. Their absorption spectra are shown in Fig. 4. From their marked splitting patterns, these two isomers are assigned as taking the *β-mer(N)-trans(Cl,* O_{adao}*)* structure.

In Fig. 4, two sets of the predicted first band components of *β-mer(N)-trans(Cl,*O_{adao}*)*-$[\text{Co(adao)(Cl)(py)}]\text{ClO}_4$ are represented with the solid arrows and the dotted arrows. The former is predicted by using the following shift parameters: $\delta(N)=+330\ \text{cm}^{-1}$, $\delta(O)=-3800\ \text{cm}^{-1}$, $\delta(Cl)=-10070\ \text{cm}^{-1}$, and $\delta(py)=-1300\ \text{cm}^{-1}$ (estimated from *trans*-$[\text{CoCl}_2(\text{py})_4]^+$ [11]). The latter is predicted by the use of new adao shift parameters, $\delta(N_{\text{adao}})=+970\ \text{cm}^{-1}$, and $\delta(O_{\text{adao}})=-5190\ \text{cm}^{-1}$. When their predicted first band components are compared with the observed ones, better correspondence is observed between the latter predicted pattern and the observed one. Then, it is attempted to estimate the value of $\delta(py)$ in $[\text{Co(adao)(Cl)(py)}]\text{ClO}_4$ by using the following equation:

$$3/4\,\delta(N_{\text{adao}}) + 1/4\,\delta(py) = 21530 - 20970 = +580\ (\text{cm}^{-1}) \qquad (3)$$

Substituting the value of $\delta(N_{\text{adao}})=+970\ \text{cm}^{-1}$ into Eq. (3), $\delta(py)$ is obtained as $-670\ \text{cm}^{-1}$.

The Structure of $[Co(adao)(H_2O)(py)]ClO_4 \cdot bcs \cdot 2H_2O$. By the use of NH_4bcs, this complex could be obtained as the crystalline form for the first time. The measurement of its circular dichroism spectrum suggests that the complex is an optically active one. Its IR spectrum in a Nujol mull shows a band due to bcs^- at $1760\ \text{cm}^{-1}$ and a strong broad band due to ClO_4^- around $1100\ \text{cm}^{-1}$.

The first absorption band of brown orange isomer exhibits a sub-peak at the lower wave number side ($\approx 18900\ \text{cm}^{-1}$) of major peak ($21790\ \text{cm}^{-1}$), as seen in Fig. 4 and Table 1. From this large splitting pattern, the isomer can be identified as the *trans(O)* one.[12,13] It is found from Fig. 1 that the coordinated adao in the *trans(O)* isomer takes necessarily the *β-mer(N)* coordination mode, and hence $[\text{Co(adao)(H}_2\text{O)(py)}]\text{ClO}_4\cdot$bcs is assigned to the *β-mer(N)-trans(O)* structure. It is an interesting behavior that the intensity of the higher wave number split component is stronger than that of the lower wave number one, which is thought to consist of two components.

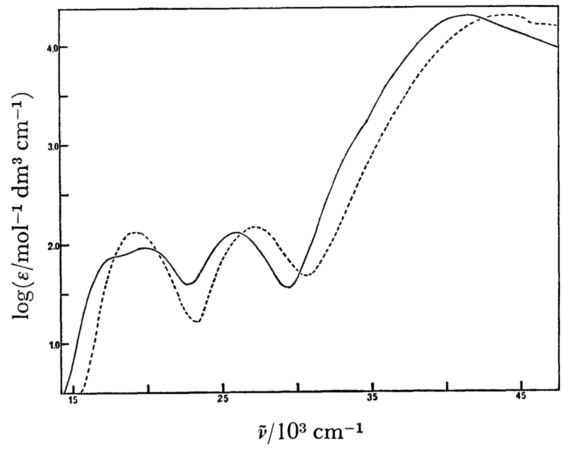

Fig. 5. The absorption spectra of $[\text{Co(adao)(Cl)(H}_2\text{O)}]\text{ClO}_4$.
——: *β-mer(N)*-$[\text{Co(adao)(Cl)(H}_2\text{O)}]\text{ClO}_4$ (deep crimson), ---: *β-fac(N)*-$[\text{Co(adao)(Cl)(H}_2\text{O)}]\text{ClO}_4$ (pink red).

In order to estimate the shift parameter of aqua ligand ($\delta(H_2O)$), new shift parameters, $\delta(N_{\text{adao}})=+970\ \text{cm}^{-1}$, $\delta(O_{\text{adao}})=-5190\ \text{cm}^{-1}$, and $\delta(py)=-670\ \text{cm}^{-1}$, are used. Then, the value of $\delta(H_2O)$ is obtained as $-4210\ \text{cm}^{-1}$.

The Structures of $[Co(adao)(Cl)(H_2O)]ClO_4$. For the aquachloro complex, two isomers, deep crimson and pink red isomers, were isolated. The elemental analyses of these isomers showed the following compositions: $[\text{Co(adao)(Cl)(H}_2\text{O)}]\text{ClO}_4$ for the deep crimson isomer, $[\text{Co(adao)(Cl)(H}_2\text{O)}]\text{ClO}_4\cdot\text{H}_2\text{O}$ for the pink red one. As seen in Fig. 5 and Table 1, the deep crimson isomer shows the first band with two split components ($\approx 17200\ \text{cm}^{-1}$ and $19830\ \text{cm}^{-1}$); the intensity of the higher wave number component is stronger than that of the lower wave number one. The pink red isomer shows the first band without splitting ($19140\ \text{cm}^{-1}$). The second absorption maximum of the deep crimson isomer is located at a lower wave number ($25830\ \text{cm}^{-1}$) than that of the pink red isomer ($27030\ \text{cm}^{-1}$).

When the configuration of *s*-N is ignored, seven geometrical isomers are possible in the complex of $[\text{Co(adao)(Cl)(H}_2\text{O)}]^+$ (in Fig. 1). In order to predict the first split components for these seven geometrical isomers, the new estimated shift parameters, $\delta(N_{\text{adao}})=+970\ \text{cm}^{-1}$, $\delta(O_{\text{adao}})=-5190\ \text{cm}^{-1}$, $\delta(H_2O)=-4210\ \text{cm}^{-1}$, which were mentioned above, and $\delta(Cl)=-10070\ \text{cm}^{-1}$,[10] are used. In Fig. 6, their predicted components are shown with the solid arrows together with the absorption spectrum of deep crimson isomer.

When the predicted split patterns are compared with the observed first band of deep crimson isomer, the predicted split patterns of three structures, *β-mer(N)-trans(Cl,*O_{adao}*)*, *β-mer(N)-cis(Cl,*O_{adao}*)*, and *trans*, agree with the split pattern of the observed first band. Among the three possible structures, the best coinci-

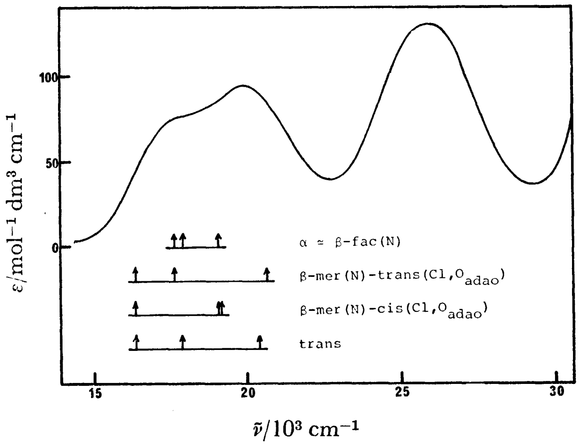

Fig. 6. The absorption spectrum of deep crimson [Co(adao)(Cl)(H_2O)]ClO_4 and the predicted first band components (solid arrows) for the possible geometrical isomers of [Co(adao)(Cl)(H_2O)]$^+$.

dence is observed between the predicted first band components of *trans* structure and the observed first band. However, the possibility of a *trans* structure is excluded, because it was already found that the treatment of this deep crimson isomer with hydrochloric acid gave only *β-mer(N)*-[Co(adao)Cl_2], as was reported in the previous paper.[1)] Furthermore, as is shown in Fig. 7, the proton NMR spectrum of deep crimson isomer shows one AB quartet in the range of 2.09 ppm to 3.18 ppm, although the two resonances at the lower field split into two doublets. The value of $\delta_{AB}(=\delta_A-\delta_B)$ is about 0.7 ppm ($J_{AB}=18$ Hz). As was reported in the previous papers,[1,7,8)] this observation of AB quartet pattern due to the adao glycinate ring protons suggests that the deep crimson isomer takes the α or the *β-mer(N)* structure. From the consideration of these proton NMR and absorption spectral patterns, the coordination mode of deep crimson isomer is assigned to the *β-mer(N)* one.

As was mentioned above, the reaction of deep crimson *β-mer(N)*-[Co(adao)(Cl)(H_2O)]ClO_4 and ammonia or pyridine gave *β-mer(N)-trans(Cl,O*$_{adao}$*)*-[Co(adao)(Cl)(NH_3)]ClO_4 or *β-mer(N)-trans(Cl,O*$_{adao}$*)*-[Co(adao)(Cl)(py)]ClO_4. These facts indicate that the chloro ligand in the deep crimson isomer occupies the *trans* position to "O$_{adao}$." Thus, it can be concluded that the structure of deep crimson isomer is the *β-mer(N)-trans(Cl,O*$_{adao}$*)* one.

In Fig. 5, the absorption spectrum of pink red isomer is shown. From the narrow first absorption band shape, it is recognized that the pink red isomer takes the α or the *β-fac(N)* structure. The proton NMR spectrum of the pink red isomer is shown in Fig. 7. The proton NMR spectrum shows the strong doublet peaks at 1.64 ppm and 1.69 ppm, due to the adao glycinate ring protons. These resonance peaks are located at higher field than those of *β-fac(N)*-[Co(adao)CO_3] (located at 2.73 ppm and 2.41 ppm) and *β-fac(N)*-[Co(adao)mal] (located at 2.35 ppm and 2.29 ppm).[8)] In the proton NMR studies of [Co(Hedta)X]$^{n-}$ (X= NO_2^- and H_2O),[14-16)] [Co(edta)en]$^-$,[17)] and [Co(H_2dtpa)NO_2]$^-$,[18)] the resonance peaks of the uncoordinated glycinate ring protons are observed as the singlet or AB quartet pattern in the field region lower than 2.0 ppm. Therefore, some doubts as to whether the adao glycinate ring in the pink red isomer is coordinated to the Co(III) ion or not, still remain.

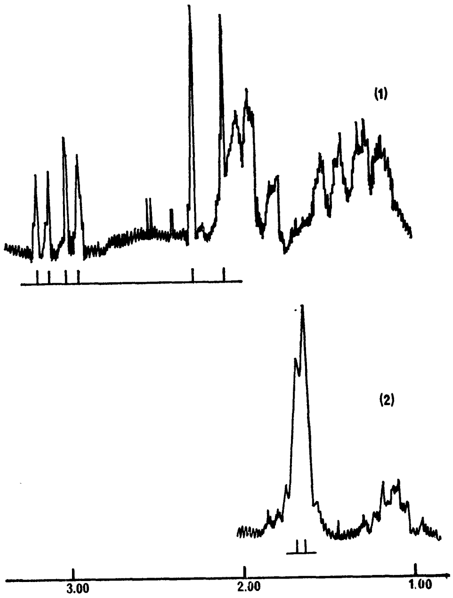

Fig. 7. The proton NMR spectra of [Co(adao)(Cl)(H_2O)]ClO_4.
(1): *β-mer(N)*-[Co(adao)(Cl)(H_2O)]ClO_4 (deep crimson), (2): *β-fac(N)*-[Co(adao)(Cl)(H_2O)]ClO_4 (pink red).

To clarify the above doubts, a few preparations using the pink red isomer had been achieved as were described in procedure (*5*) and the previous paper.[1)] Their isolated complexes have the compositions of [Co(adao)(Cl)(NO_2)] and [Co(adao)Cl_2]. From the facts, it is inferred that the adao glycinate ring is coordinated to the Co(III) ion. As the other experiment, the chromatographic separation was also performed (Method C in *2*). The chromatographic behavior of pink red isomer was similar to that of *β-mer(N)*-[Co(adao)(Cl)(H_2O)]ClO_4. This fact suggests that the pink red isomer is an univalent cation and that the adao glycinate ring is not free. Then, the pink red isomer is tentatively assigned to the *β-fac(N)* structure. However, it is difficult to decide the position of the chloro ligand in the pink red isomer.

The Structure of [Co(adao)(NO_2)(H_2O)]ClO_4. The reaction of orange yellow *β-mer(N)*-[Co(adao)$(NO_2)_2$][1)] and $HClO_4$ gave [Co(adao)(NO_2)(H_2O)]ClO_4. The reaction of α-[Co(adao)$(NO_2)_2$][1)] and $HClO_4$ was attempted, but no crystalline complex could be obtained. In Fig. 8, the absorption spectrum of [Co(adao)(NO_2)(H_2O)]ClO_4 is shown.

The proton NMR spectrum of [Co(adao)(NO_2)(H_2O)]ClO_4 shows one AB quartet pattern at 2.01, 2.19, 2.81, and 2.99 ppm. From this observation, the adao coordination mode is the α or the *β-mer(N)* one. The reaction of α-[Co(adao)$(NO_2)_2$] and $HClO_4$ gave no crystals. The structure can thus be assigned to the *β-mer(N)* one. For *β-mer(N)*-[Co(adao)(NO_2)-

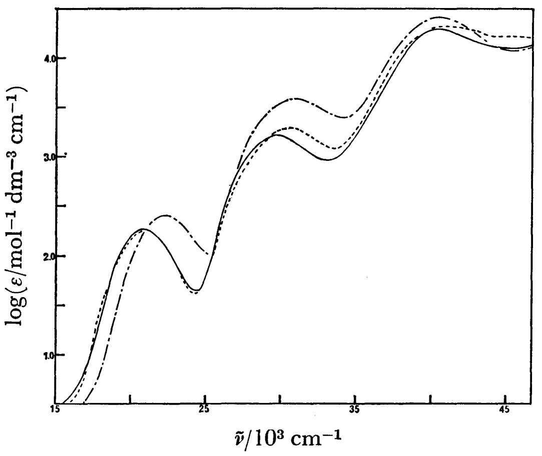

Fig. 8. The absorption spectra of $[Co(adao)(NO_2)(H_2O)]ClO_4$ and $[Co(adao)(Cl)(NO_2)]$.
——: *β-mer(N)*-$[Co(adao)(NO_2)(H_2O)]ClO_4$ (red orange), - - -: *β-fac(N)*-$[Co(adao)(Cl)(NO_2)]$ (red orange), —·—: *β-mer(N)*-$[Co(adao)(NO_2)_2]$ (orange yellow).

$(H_2O)]ClO_4$, the *cis(O)* and *trans(O)* isomers are possible. When $[Co(adao)(NO_2)(H_2O)]ClO_4$ is regarded as a complex of $[CoN_4O_2]$ type, the *trans(O)* isomer shows the more split first absorption band than that of the *cis(O)* one.[12,13] Because the isolated aquanitro isomer exhibits the first absorption band with no remarkable splitting, it is concluded that $[Co(adao)(NO_2)(H_2O)]ClO_4$ takes the *β-mer(N)-cis(O)* structure. The production of *β-mer(N)-cis(O)*-$[Co(adao)(NO_2)(H_2O)]ClO_4$ by the treatment of $[Co(adao)(NO_2)_2]$ with $HClO_4$ indicates that the reactivities of two nitro ligands in *β-mer(N)*-$[Co(adao)(NO_2)_2]$ are different.

The Structure of $[Co(adao)(Cl)(NO_2)]$. As was mentioned in (*5*), $[Co(adao)(Cl)(NO_2)]$ was obtained as the slightly soluble crystal from *β-fac(N)*-$[Co(adao)(Cl)(H_2O)]ClO_4$ by the treatment with $NaNO_2$. Table 1 ($\varepsilon=2000$ for the chloronitro complex and $\varepsilon=1652$ for the aquanitro one) shows that the isolated complex contains one coordinated nitro ligand. It is also observed that its first absorption maximum is located at a similar wave number region to that of *β-mer(N)-cis(O)*-$[Co(adao)(NO_2)(H_2O)]ClO_4$. The similar absorption band shifts to the higher wave number side are observed as an anomalous absorption spectral behavior also in the other *β-fac(N)* complexes.

Furthermore, it was found that the treatment of $[Co(adao)(Cl)(NO_2)]$ with $HClO_4$ gave *β-fac(N)*-$[Co(adao)(Cl)(H_2O)]ClO_4$. The fact suggests that the reaction of *β-fac(N)*-$[Co(adao)(Cl)(H_2O)]ClO_4$ and $NaNO_2$ proceeds with the configurational retention of adao. This retention reaction supports that the isolated chloronitro isomer takes the *β-fac(N)* structure.

Summary. From the successful isolations of two isomers of *β-mer(N)-trans*(Cl,O_{adao})-$[Co(adao)(Cl)(NH_3)]ClO_4$, reddish brown, pale brown, and two isomers of *β-mer(N)-trans*(Cl,O_{adao})-$[Co(adao)(Cl)(py)]ClO_4$, reddish brown, dull reddish brown, the existence of two kinds of *β-mer(N)* isomers with the different *s*-N configurations was proved.

By using their definitive split first band maxima, furthermore, the shift parameters of the adao ligating atoms were estimated as $\delta(N_{adao})=+970\ cm^{-1}$ and $\delta(O_{adao})=-5190\ cm^{-1}$ at present. The pyridine shift parameter ($\delta(py)=-670\ cm^{-1}$) and the aqua one ($\delta(H_2O)=-4210\ cm^{-1}$) could also be calculated. On the basis of the absorption band components predicted by the use of these shift parameters and the considerations of the preparative results, the deep crimson $[Co(adao)(Cl)(H_2O)]ClO_4$ could be assigned to the *β-mer(N)-trans*(Cl,O_{adao}) structure.

Besides the one kind of isolated *β-fac(N)*-$[Co(adao)Cl_2]$,[1] it was also found that the respective *β-fac(N)* isomers can be isolated in $[Co(adao)(Cl)(H_2O)]ClO_4$ and $[Co(adao)(Cl)(NO_2)]$.

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2) The following abbreviations are used for ligands: adao ($^-OOCCH_2NHCH_2CH_2NHCH_2CH_2NH_2$), 8-amino-3,6-diazaoctanate; edta, ethylenediaminetetraacetate; dtpa, diethylenetriaminepentaacetate; en, ethylenediamine; py, pyridine; bcs, $(+)_{589}$-(1*R*,3*S*,4*S*,7*R*)-3-bromocamphor-9-sulfonate.

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