September, 1983] © *1983 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, ***56***, *2839—2840 (1983)* 2839

# Studies of the Cobalt(III) Complexes of 8-Amino-3,6-diazaoctanate Ion. V.[1] Optical Resolutions and Circular Dichroism Spectra of 8-Amino-3,6-diazaoctanato(glycinato)cobalt(III) Perchlorates

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**Synopsis.** Three optically active isomers, $(+)_{589}$-, $(-)_{589}$-*cis(O)*-, and $(-)_{589}$-*trans(O)*-[Co(adao)(gly)]$ClO_4$, where adao and gly stand for 8-amino-3,6-diazaoctanate and glycinate, have been obtained. The structures have been determined on the basis of the absorption, circular dichroism, and proton NMR spectra.

All cobalt(III) complexes with 8-amino-3,6-diazaoctanate (adao)[2] are chiral, but the resolution has not been reported except for [Co(adao)(en)]$Cl_2$.[2,3] Therefore, it is significant to obtain the optically active isomers to clarify the relationship between the structures and circular dichroism (CD) spectra.

## Experimental

*Resolutions.* *(1) $(+)_{589}$- and $(-)_{589}$-*cis(O)-*[Co(adao)(gly)]$ClO_4$:* *cis(O)*-[Co(adao)(gly)]$ClO_4$[4] was transformed into the chloride form by passing the solution through a column of an anion exchanger (Dowex 1-X8, $Cl^-$ form). Orange red crystals pptd. by adding ethanol to the eluate were collected on a filter and washed with ethanol, ether in turn.

The *cis(O)*-[Co(adao)(gly)]Cl (3.28 g) was dissolved in 10 $cm^3$ of water and then $NH_4$bcs (1.64 g)[2] was added. The mixture was warmed at 45 °C for 5 min. Orange red crystals appeared were collected, and washed with an ethanol–ether mixture (1 : 1), and ether. The yield of diastereoisomeric salt was 2.07 g. The filtrate (named as F-A) was reserved for the isolation of the antipodal isomer.

The diastereoisomeric salt (2.0 g) was suspended in 20 $cm^3$ of water, and after adding 5 $cm^3$ of 6 M (1 M = 1 mol $dm^{-3}$) $HClO_4$, the suspension was heated at 65 °C for 5 min. Orange red crystals appeared were filtered and washed with ethanol. The yield was 1.1 g. After the crystals were extracted with two 10 $cm^3$ portions of hot water (70 °C), the third extract with 20 $cm^3$ of hot water was cooled. The crystals deposited from the third extract were collected and washed with ethanol. The optically active isomer showed positive optical rotation at 589 nm. The yield of $(+)_{589}$-*cis(O)*-[Co(adao)(gly)]$ClO_4\cdot H_2O$ (named as **1a**) was about 0.5 g. Found: C, 23.24; H, 5.10; N, 13.77%. Calcd for [Co(adao)(gly)]$ClO_4\cdot H_2O = CoC_8H_{20}N_4O_9Cl$: C, 23.40; H, 4.91; N, 13.64%.

The F-A was concentrated to 5 $cm^3$ at 40 °C. After cooling, the precipitate was filtered off. To the filtrate was added 2 $cm^3$ of 6 M $HClO_4$, and the mixture was cooled. The crystals deposited were collected and washed with ethanol. The yield was 1.7 g. Recrystallization was carried out with the same method mentioned above. This enantiomer showed negative optical rotation at 589 nm. The yield of $(-)_{589}$-*cis(O)* enantiomer (named as **1b**) was 0.7 g.

*(2) $(-)_{589}$-*trans(O)-*[Co(adao)(gly)]$ClO_4$:* By using a similar method mentioned in *(1)*, *trans(O)*-[Co(adao)(gly)]Cl was obtained from *trans(O)*-[Co(adao)(gly)]$ClO_4$.[4]

Silver oxide obtained from $AgNO_3$ (0.84 g) and 5 $cm^3$ of 1 M NaOH was added to a solution of $(+)_{589}$-tartaric acid (0.75 g) in 5 $cm^3$ of water, and the mixture was stirred at 65 °C for 5 min. To the suspension was added a solution of *trans(O)*-[Co(adao)(gly)]Cl (1.64 g) in 10 $cm^3$ of water. The mixture was heated at 65 °C for 5 min and cooled. After the removal of AgCl, the filtrate was concentrated to 3 $cm^3$. The solution was kept in a refrigerator overnight and the precipitate was filtered off. After the addition of a small amount of ethanol, the mixture was left in a refrigerator again for two months, whereupon one large red crystal deposited out. The crystal was separated from the mother liquor, and then washed with ethanol, and ether. The yield of diastereoisomeric salt was 0.8 g.

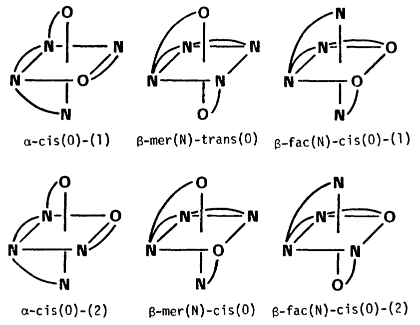

Fig. 1. The possible *Δ* enantiomers of [Co(adao)(gly)]$^+$.

After the diastereoisomeric salt (0.8 g) was dissolved in 1 $cm^3$ of water, two drops of 6 M $HClO_4$ were added. Red crystals appeared. After cooling, the crystals were collected and washed with ethanol–ether (1 : 1). The optically active isomer showed negative optical rotation at 589 nm. Furthermore, its absorption (AB) spectrum was exactly the same as that of the racemic *trans(O)*-[Co(adao)(gly)]$ClO_4$.[4] The yield of $(-)_{589}$-*trans(O)*-[Co(adao)(gly)]$ClO_4$ (named as **2**) was 0.5 g.

*Measurements.* The AB and $^1$H NMR spectra were recorded with similar methods reported in the previous paper.[1] The optical rotations and CD spectra were measured by a JASCO DIP-180 polarimeter and JASCO MOE-1 spectropolarimeter, respectively.

## Results and Discussion

*The Structures of [Co(adao)(gly)]$ClO_4$.* As glycinate is an unsymmetrical N–O type ligand, [Co(adao)(gly)]$^+$ belongs to a type of [$CoN_4O_2$]. Without consideration of the adao's secondary amine (*s*-N) configurations, [Co(adao)(gly)]$^+$ has twelve optically active isomers (Fig. 1).

In Fig. 2 the AB spectra of **1a**, **1b**, and **2** are shown along with their CD ones. It is known that the first AB band of *trans(O)* isomer is more split than that of *cis(O)* in a type of [$CoN_4O_2$].[4–6] On the basis of their first AB band shapes, **1a** and **1b** can be assigned to the *cis(O)* structure, and **2**, to the *trans(O)*. From Fig. 1 it is apparent that the adao coordination mode in **2** is the *β-mer(N)*. However, it is difficult to determine the adao coordination modes in **1a** and **1b** from the AB spectra alone. The $^1$H NMR spectra of **1a** and **2** showed similar quartet patterns: for **1a**, (1.76, 1.93, 2.69, 2.86 ppm), and for **2**, (1.86, 2.03, 2.83, 3.00 ppm). This indicates that the adao's glycinate ring takes the apical disposition in these isomers,[1,4,7] and that **1a** takes the *α* or the *β-mer(N)* structure,

TABLE 1. AB AND CD SPECTRAL DATA OF $[Co(adao)(gly)]ClO_4$

| | AB<br>$\tilde{\nu}_{max}$/cm$^{-1}$<br>($\varepsilon$/mol$^{-1}$ dm$^3$ cm$^{-1}$) | CD<br>$\tilde{\nu}_{ext}$/cm$^{-1}$<br>($\Delta\varepsilon$/mol$^{-1}$ dm$^3$ cm$^{-1}$) |
|---|---|---|
| $\Lambda$-$(+)_{589}$-*β-mer(N)-cis(O)*- | 20000 (172) | 19000 (+1.18) |
| $[Co(adao)(gly)]ClO_4$ | | 21600 (+0.51) |
| (orange red) | 27860 (142) | 25500 (+0.14) |
| | | 28170 (−0.33) |
| $\Delta$-$(-)_{589}$-*β-mer(N)-cis(O)*- | 20000 (172) | 19000 (−1.35) |
| $[Co(adao)(gly)]ClO_4$ | | 21360 (−0.59) |
| (orange red) | 27860 (142) | 25500 (−0.17) |
| | | 28170 (+0.36) |
| $\Delta$-$(-)_{589}$-*β-mer(N)-trans(O)*- | 18940 (102) | 18600 (−0.09) |
| $[Co(adao)(gly)]ClO_4$ | 20300 ( —) | 22000 (−0.36) |
| (red)$^{a)}$ | 27870 (153) | 28000 (+0.19) |

a) Partial resolution.

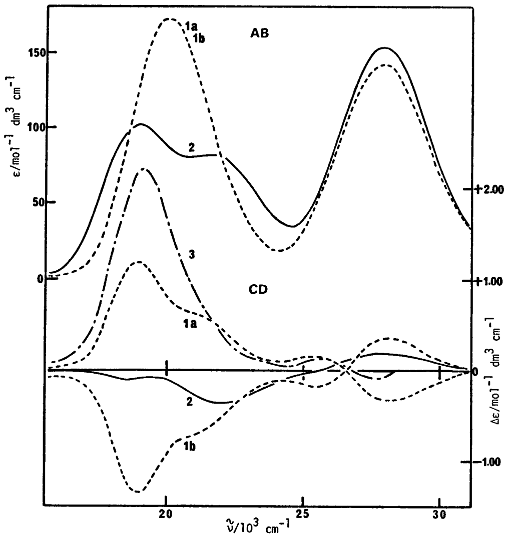

Fig. 2. The absorption (AB) and circular dichroism (CD) spectra.
----: $\Lambda$-*β-mer(N)-cis(O)*-$[Co(adao)(gly)]ClO_4$ (**1a**),
----: $\Delta$-*β-mer(N)-cis(O)*-$[Co(adao)(gly)]ClO_4$ (**1b**),
——: $\Delta$-*β-mer(N)-trans(O)*-$[Co(adao)(gly)]ClO_4$ (**2**),
———: $\Lambda$-$C_1$-*cis(O)*-$[Co(gly)_2(en)]I$ (**3**).

The CD curve of **1a** in the first AB band region shows two positive peaks (Fig. 2). The CD curve of **1b** is the mirror image to that of **1a**. The fact suggests that **1a** and **1b** are enantiomers. It is well known that the absolute configuration of a cobalt(III) complex with three bidentate ligands, in which each bidentate ligand forms a five membered chelate ring, can be assigned from the sign of major CD peak in the first AB band region, *i.e.*, the $\Lambda$ complex has (+) major CD peak, and the $\Delta$ complex has (—) one.[8-12] By applying this empirical rule, **1a** and **1b** can be assigned to $\Lambda$ and $\Delta$ structure, respectively.

The chelate ring pairs of $\Lambda$-*α-cis(O)-(1)*- and $\Lambda$-*β-mer(N)-cis(O)*-$[Co(adao)(gly)]^+$ are compared with those of $\Lambda$-$C_1$-*cis(O)*-$[Co(gly)_2(en)]I$ (named as **3**)[11] having the same *cis(O)*-$[CoN_4O_2]$ chromophore (Fig. 3). **3** and $\Lambda$-*α-cis(O)-(1)*-$[Co(adao)(gly)]^+$ have $\Lambda\Lambda\Lambda$ chelate ring pairs and $\Lambda$-*β-mer(N)-cis(O)*-$[Co(adao)(gly)]^+$ has $\Lambda\Lambda\Lambda\Delta$ (net 2$\Lambda$). When **1a** takes the $\Lambda(\Lambda\Lambda\Lambda)$-*α* structure, its CD strength is expected to be similar to that of **3**. When **1a** takes the $\Lambda(\Lambda\Lambda\Lambda\Delta)$-*β-mer(N)* structure, its CD strength is expected to be smaller than that of **3**. The CD strength of **3** is stronger than that of **1a**, as seen in Fig. 2. Therefore, it is appropriate to assign tentatively **1a** to the $\Lambda(\Lambda\Lambda\Lambda\Delta)$-*β-mer(N)-cis(O)* structure, and **1b** to the $\Delta(\Delta\Delta\Delta\Lambda)$-*β-mer(N)-cis(O)* one.

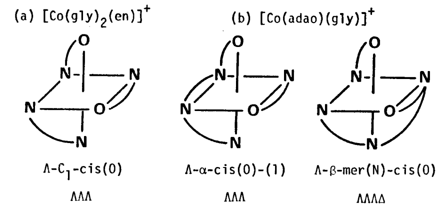

Fig. 3. The comparison of chelate ring pairs among $\Lambda$-$C_1$-*cis(O)*-$[Co(gly)_2(en)]^+$, $\Lambda$-*α-cis(O)-(1)*-$[Co(adao)(gly)]^+$, and $\Lambda$-*β-mer(N)-cis(O)*-$[Co(adao)(gly)]^+$.

In the chromatographic separation of reaction product of *β-mer(N)*-$[Co(adao)(Cl)(H_2O)]ClO_4$ and gly,[2] one *trans(O)* (red) and two *cis(O)* (orange red, pink red) racemic isomers were detected. The yield of the orange red isomer was higher than that of the pink red. It was reported that under weak alkaline conditions using *β-mer(N)*-$[Co(adao)(Cl)(H_2O)]ClO_4$ as the starting material, the yield of *α* isomer is lower than that of *β-mer(N)*.[1,7,13] Thus, the orange red *cis(O)* isomer can be assigned to the *β-mer(N)* structure. This chromatographic behavior supports the above assignments for the optically active *cis(O)* isomers.

The CD spectrum of **2** is shown in Fig. 2. From the two negative CD peaks in the first AB band region,[9-12] **2** is assignable to the $\Delta(\Delta\Delta\Delta)$ structure. Because of the weak CD strength, however, **2** seems to have been obtained as the partially resolved isomer. These AB and CD spectral data are summarized in Table 1.

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2) The following abbreviations are used for the ligands: adao, 8-amino-3,6-diazaoctanate; gly, glycinate; bcs, $(+)_{589}$-(1*R*, 3*S*, 4*S*, 7*R*)-3-bromocamphor-9-sulfonate; en, ethylenediamine.

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