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# Circular Dichroism of Mixed Biguanide Ethylenediamine Cobalt(III) Complexes

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Two kinds of mixed biguanide ethylenediamine complexes, $[Co(bgH)_2(en)]Cl_3 \cdot 3H_2O$ and $[Co(bgH)(en)_2]Cl_3 \cdot 2H_2O$, have been resolved into their optically active isomers. The circular dichroism spectra of a complete series of the mixed complexes, $(-)_{589}$-$[Co(bgH)_3]^{3+}$, $(+)_{589}$-$[Co(bgH)_2(en)]^{3+}$, $(+)_{589}$-$[Co(bgH)(en)_2]^{3+}$, and $(+)_{589}$-$[Co(en)_3]^{3+}$, have been investigated in neutral and alkaline aqueous solutions. In alkaline solutions, the circular dichroism and absorption curves of the biguanide complexes shift to longer wavelengths than those in neutral solutions; this may be caused by the change of the coordinated biguanide (bgH) to the uninegative ligand ($bg^-$) by deprotonation. A mixed guanylurea complex, $[Co(guH)(en)_2]Cl_3 \cdot 2H_2O$, has been newly prepared and optically resolved.

Biguanide, $NH\{C(NH_2)NH\}_2$=bgH,1) combines with many kinds of transition metal salts to give a variety of coordination compounds with six-membered chelate rings,2–4) of which cobalt(III) and chromium(III) complexes have recently been noted in terms of the circular dichroism (CD) spectra and absolute configuration.5,6) Michelsen,5) for example, suggested that $(-)_{589}$-$[Co(bgH)_3]^{3+}$ and $(-)_{589}$-$[Cr(bgH)_3]^{3+}$ have an absolute configuration $\Lambda$,7) comparing the CD behavior of the complexes in the so-called first absorption band region with that of $\Lambda(+)_{589}$-$[Co(en)_3]^{3+}$, whose absolute configuration was unequivocally determined by an X-ray technique.8) Recently, Brubaker and Webb6) determined the absolute configuration of the $(-)_{589}$-$[Cr(bgH)_3]^{3+}$ to be $\Lambda$ on the basis of X-ray analysis of the *d*-10-camphorsulfonate and suggested that the $(-)_{589}$-$[Co(bgH)_3]^{3+}$ should have $\Delta$ configuration, from the comparison of the ultraviolet CD spectra of the cobalt(III) and chromium(III) complexes. Thus, the conclusions from the CD of *d–d* absorption band region and of ultraviolet ligand absorption band region completely contradict each other for the tris-biguanide complex of cobalt(III).

In these circumstances, it is thought to be desirable to study more systematically the CD spectra of mixed complexes of ethylenediamine and biguanide, namely, $[Co(bgH)_3]^{3+}$, $[Co(bgH)_2(en)]^{3+}$, $[Co(bgH)(en)_2]^{3+}$, and $[Co(en)_3]^{3+}$. In the present paper, preparations and optical resolutions of such complexes and their absorption and CD spectra are reported. In the course of this study, a new guanylurea cobalt(III) complex, $[Co(guH)(en)_2]^{3+}$, happened to be obtained, where guH stands for a guanylurea molecule $NH(NH_2)CNHCO(NH_2)$.

## Experimental

*Preparation and Optical Resolution.* *$[Co(bg)_3] \cdot 2H_2O$ and $[Co(bgH)_3]Cl_3$*: These complexes were prepared by the method of Ray and Dutt.9)

Found: C, 18.82; H, 5.76; N, 54.08%. Calcd for $C_6H_{18}N_{15}Co \cdot 2H_2O = [Co(bg)_3] \cdot 2H_2O$: C, 18.23; H, 5.62; N, 53.15%.

Found: C, 15.95; H, 4.70; N, 44.97%. Calcd for $C_6H_{21}N_{15}Cl_3Co = [Co(bgH)_3]Cl_3$: C, 15.37; H, 4.53; N, 44.84%.

*$(-)_{589}$-$[Co(bgH)_3]Cl_3$*: The optical resolution was carried out by the method of Ray and Dutt.10) $[\alpha]^{13}_{589} = -450°$, $[M]^{13}_{589} = -2110°$.

*$[Co(bgH)_2(en)]Cl_3 \cdot 3H_2O$*: The chloride was obtained

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1) The abbreviations, bgH and bg, represent a biguanide molecule and a deprotonated biguanide (uninegative ion), respectively.

2) P. Ray, *Chem. Rev.*, **61**, 313 (1961).

3) D. Sen, *J. Chem. Soc., A*, **1969**, 2900.

4) R. L. Dutta, *J. Indian Chem. Soc.*, **44**, 863 (1967).

5) K. Michelsen, *Acta Chem. Scand.*, **19**, 1175 (1965).

6) G. R. Brubaker and L. E. Webb, *J. Amer. Chem. Soc.*, **91**, 7199 (1969).

7) The symbols $\Delta$ and $\Lambda$ are used for absolute configurations of the tris or bis chelate type metal complexes, according to a tentative proposal by the Commission on the Nomenclature of Inorganic Chemistry of the IUPAC: *Inorg. Chem.*, **9**, 1 (1970).

8) Y. Saito, *Pure Appl. Chem.*, **17**, 21 (1968).

9) P. Ray and N. K. Dutt, *J. Indian Chem. Soc.*, **16**, 621 (1939).

10) P. Ray and N. K. Dutt, *ibid.*, **18**, 289 (1941).

by converting the known sulfate[11] with barium chloride. This complex was also prepared by the reaction of K[Co-$(CO_3)_2$(en)][12] and biguanide sulfate monohydrate. The complex is very soluble in water.

Found: C, 15.11; H, 5.97; N, 34.61%. Calcd for $C_6H_{22}N_{12}Cl_3Co\cdot 3H_2O$=[Co(bgH)$_2$(en)]$Cl_3\cdot 3H_2O$: C, 14.96; H, 5.87; N, 34.90%.

*$(-)_{589}$- and $(+)_{589}$-[Co(bgH)$_2$(en)]$Cl_3\cdot H_2O$*: To a solution containing 4.3 g of $(\pm)$-[Co(bgH)$_2$(en)]$Cl_3\cdot 3H_2O$ in 20 m*l* of hot water (70°C) was added with stirring a solution of 5.0 g of potassium di-*μ*-L-tartrato(4-)diantimonate-(III) trihydrate, $K_2[Sb_2(d\text{-}C_4H_2O_6)_2]\cdot 3H_2O$, in 30 m*l* of hot water (70°C). After the solution had been kept at room temperature for about an hour, the diastereomer deposited was filtered (the filtrate was used for the isolation of $(+)_{589}$ isomer) and washed with ice-water, ethanol and then ether. The diastereomer which was obtained in yellow crystals was recrystallized from hot water. $[\alpha]^{20}_{589}=+100°$.

To a suspension of 2.0 g of the diastereomer in 20 m*l* of water was added 3.5 g of powdered barium chloride dihydrate with vigorous stirring, and then 100 m*l* of ethanol was added to the resulted solution. After the solution had been kept in an ice-bath, the resulted precipitate was filtered off. The filtrate was evaporated to dryness in a vacuum evaporator at room temperature. The orange-colored residue was recrystallized from a small amount of water by adding ethanol-acetone (1 : 1) mixture and then acetone, and dried in air. $[\alpha]^{20}_{589}=-93°$, $[M]^{20}_{589}=-415°$.

$(+)_{589}$-[Co(bgH)$_2$(en)]$Cl_3\cdot H_2O$ was obtained from the filtrate described above.

Found: C, 16.33; H, 5.58; N, 37.43%. Calcd for $C_6H_{22}N_{12}Cl_3Co\cdot H_2O$=$(+)_{589}$-[Co(bgH)$_2$(en)]$Cl_3\cdot H_2O$: C, 16.17; H, 5.44; N, 37.72%. $[\alpha]^{20}_{589}=+93°$, $[M]^{20}_{589}=+415°$.

*[Co(bgH)(en)$_2$]$Cl_3\cdot 2H_2O$*: The preparation of this complex was carried out by a modified procedure of Dutta's method.[4] A solution containing 7.6 g of biguanide sulfate monohydrate in 200 m*l* of water was added to 150 m*l* aqueous solution of 11.1 g of barium hydroxide octahydrate. After the resulted barium sulfate had been filtered off, the filtrate was added to a solution containing 10 g of *trans*-[Co(Cl)$_2$-(en)$_2$]Cl in 100 m*l* of water. The solution was heated on a water bath for 8 hr at 55°C. The color of the solution changed from purple to orange red. When the solution was concentrated to about 80 m*l* with a vacuum evaporator at 33°C, the orange crystals, [Co(bgH)$_3$]$Cl_3$, began to appear. After the solution was kept in an ice-bath for about an hour, the crystals were removed by filtration. The filtrate was concentrated to 25 m*l* in a vacuum evaporator and allowed to stand at room temperature for several days. The crude orange red complex was filtered and washed with ethanol and then ether. Yield: 5.7 g. The crude product was recrystallized from hot water by adding ethanol-acetone (1 : 1) mixture.

Found: C, 17.01; H, 6.73; N, 29.89%. Calcd for $C_6H_{23}N_9Cl_3Co\cdot 2H_2O$=[Co(bgH)(en)$_2$]$Cl_3\cdot 2H_2O$: C, 17.05; H, 6.45; N, 29.83%.

*$(-)_{589}$-[Co(bgH)(en)$_2$]$Cl_3\cdot 3H_2O$*: The racemate, $(\pm)$-[Co(bgH)(en)$_2$]$Cl_3\cdot 2H_2O$, (2.0 g), was dissolved in 15 m*l* of hot water. To this solution was added a solution containing 2.37 g of potassium di-*μ*-L-tartrato(4-)diantimonate(III) trihydrate in 25 m*l* of hot water with stirring. The mixed solution was kept at room temperature for a few min to complete the crystallization. The less soluble diastereomer was obtained in light orange powder. $[\alpha]^{15}_{589}=-96°$.

One gram of the diastereomer, 3 g of barium chloride dihydrate and 10 m*l* of water was triturated in a mortar. The white precipitate resulted was filtered off. Fifty milliliters of ethanol was added to the filtrate and the white precipitate was filtered off again. After the filtrate had been concentrated to 4 m*l* in a vacuum evaporator at 28°C, 2 m*l* of ethanol-acetone (1 : 1) mixture was added to it. The white precipitate was filtered off once again. Then the filtrate was concentrated to 3 m*l* in the same way. After 12 m*l* of ethanol-acetone (1 : 1) mixture had been added to the solution, the orange red crystals desired were separated by filtration. Recrystallization of this complex was carried out from 2 m*l* of water by adding ethanol-acetone (1 : 1) mixture. The complex obtained was washed with ethanol and ether.

Found: C, 16.60; H, 6.45; N, 28.81%. Calcd for $C_6H_{23}N_9Cl_3Co\cdot 3H_2O$=$(-)_{589}$-[Co(bgH)(en)$_2$]$Cl_3\cdot 3H_2O$: C, 16.34; H, 6.64; N, 28.61%. $[\alpha]^{15}_{589}=-352°$, $[M]^{15}_{589}=-1551°$.

*[Co(guH)(en)$_2$]$Br_3$ and [Co(guH)(en)$_2$]$Cl_3\cdot 2H_2O$*: The suspension of 10 g of [Co($CO_3$)(en)$_2$]$ClO_4$ and 6.5 g of biguanide sulfate monohydrate in 20 m*l* of water was heated on a water bath for about 30 min. To the hot solution was added 15 m*l* of perchloric acid (20%) with constant stirring and the solution was heated on a water bath for 2 hr. After cooling the resulted solution to room temperature, 16 g of powdered sodium bromide was dissolved into it. The orange crystals deposited were collected by filtration, and washed with water-ethanol (1 : 1) mixture, ethanol and then ether. The crude complex was recrystallized from hot water. As described in the Results and Discussion section, it was shown that during the reaction, the biguanide employed was hydrolyzed and changed into a guanylurea.

Found: C, 13.83; H, 4.31; N, 21.48%. Calcd for $C_6H_{22}N_8OBr_3Co$=[Co(guH)(en)$_2$]$Br_3$: C, 13.83; H, 4.26; N, 21.51%.

This bromide was converted to the chloride by treating it with silver chloride.

Found: C, 17.05; H, 6.38; N, 26.53%. Calcd for $C_6H_{22}N_8OCl_3Co\cdot 2H_2O$=[Co(guH)(en)$_2$]$Cl_3\cdot 2H_2O$: C, 17.01; H, 6.20; N, 26.45%.

*$(-)_{589}$-[Co(guH)(en)$_2$]$(HO_3)_3$*: Twenty and eight-tenths grams of $(\pm)$-[Co(guH)(en)$_2$]$Br_3$ was dissolved in 40 m*l* of warm water. To this solution was rapidly added a solution containing 20 g of potassium di-*μ*-L-tartrato(4-)diantimonate(III) trihydrate in 60 m*l* of hot water (70°C) with vigorous stirring. After the solution had been chilled in an ice-bath, the light orange needle crystals deposited were filtered, and washed with cold water, ethanol and then ether. Recrystallization was carried out from hot water. The diastereomer obtained was sparingly soluble in water. $[\alpha]^{20}_{589}=-142°$.

A mixture of the diastereomer (10 g), silver nitrate (10 g) and warm water (30 m*l*) was ground enough in a mortar. The resulted precipitate was filtered off and washed twice with a small amount of water. The combined washings and filtrate was evaporated to dryness with a vacuum evaporator at room temperature. The orange-colored residue was recrystallized from hot water. The orange needle crystals deposited were filtered, and washed with a little amount of ice-water, water-ethanol (1 : 1) mixture, absolute ethanol and then ether, and dried in air.

Found: C, 15.37; H, 4.81; N, 33.19%. Calcd for $C_6H_{22}N_{11}O_{10}Co$=$(-)_{589}$-[Co(guH)(en)$_2$]$(NO_3)_3$: C, 15.42; H, 4.75; N, 32.98%. $[\alpha]^{20}_{589}=-480°$, $[M]^{20}_{589}=-2243°$.

*Measurements.* The electronic absorption spectra were measured by Shimadzu spectrophotometer QR-50. The CD spectra were recorded with a Roussel-Jouan dichrograph

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[11] R. L. Dutta and S. Sarkar, *Sci. Cult.* (Calcutta), **30**, 549 (1964).

[12] M. Mori, M. Shibata, E. Kyuno, and K. Hoshiyama, This Bulletin, **31**, 291 (1958).

and the optical rotatory dispersions were checked with Yanagimoto Recording spectropolarimeter model-185. The CD measurements were made in aqueous and 0.10 N and 0.25 N NaOH aqueous solutions. In 0.25 N NaOH aqueous solutions, $(+)_{589}$-$[Co(bgH)_2(en)]^{3+}$ and $(-)_{589}$-$[Co(bgH)(en)_2]^{3+}$ were not racemized and the racemization of $(-)_{589}$-$[Co(bgH)_3]^{3+}$ in 0.10 N NaOH aqueous solution was negligible during the CD measurement. The CD curves and data for the $(-)_{589}$-$[Co(bgH)(en)_2]^{3+}$ and $(-)_{589}$-$[Co(guH)(en)_2]^{3+}$ and of their deprotonated species are presented in reverse signs in Results and Discussion Section, Table 2, and Figs. 1—4, for the convenience of comparison with those of the other complexes; therefore the CD curves and data are refered as those for the $(+)_{589}$ isomers.

## Results and Discussion

### 1. *The Absorption and CD Spectra of Ethylenediamine-Biguanide Cobalt(III) System.*

The first absorption bands of the biguanide complexes are shifted to the longer wavelength side and are more intense than that of $[Co(en)_3]^{3+}$ (Fig. 1 and Table 1). In this region, $(+)_{589}$-$[Co(bgH)_2(en)]^{3+}$ and $(-)_{589}$-$[Co(bgH)_3]^{3+}$ in water exhibit two CD bands, one negative and another positive listing from the longer wavelength side, whereas $(+)_{589}$-$[Co(bgH)(en)_2]^{3+}$ shows only a positive CD band which is more intense than the positive $E_a$ CD component of $(+)_{589}$-$[Co(en)_3]^{3+}$ (Table 2). In the second absorption band region, all the biguanide complexes show negative CD bands in contrast to the $(+)_{589}$-tris(ethylenediamine) complex which shows a positive one. In the shorter wavelength region, the absorption spectra of the present complexes are similar to each other on the whole (Fig. 1 and Table 1). In the tris- and bis-biguanide complexes, it seems that the intense absorption bands which locate at the shorter wavelength than 250 mμ are due to $\pi$–$\pi^*$ transitions of the coordinated biguanide ligand; the CD spectra in the corresponding region show two oppositely signed CD bands, and these are very intense only when two or three biguanide ligands coordinate to a cobalt(III) ion (Figs. 2 and 3, and Table 2). Brubaker and Webb suggested that such CD band splitting in this region may be interpreted as the exciton splitting, of which a theory has been recently developed mainly by Mason,[13] Bosnich,[14] and others,[15] and that the $(-)_{589}$-$[Co(bgH)_3]^{3+}$ complex which exhibits a negative CD component at lower energy has $\Delta$ configuration. This suggestion, however, seems to contradict with a conclusion from the behavior in the d–d absorption band region (see later section 3). The absorption bands

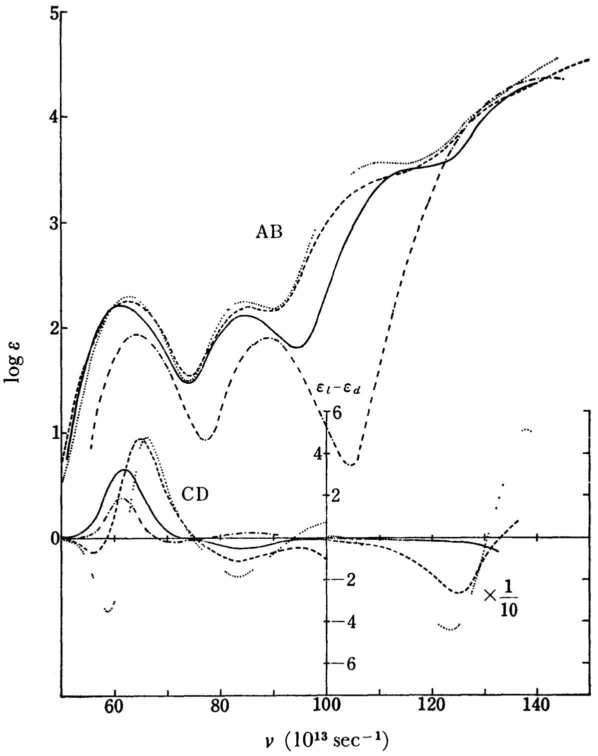

Fig. 1. Absorption (AB) and CD curves of $(-)_{589}$-$[Co(bgH)_3]^{3+}$ (……), $(+)_{589}$-$[Co(bgH)_2(en)]^{3+}$ (----), $(+)_{589}$-$[Co(bgH)(en)_2]^{3+}$ (——), and $(+)_{589}$-$[Co(en)_3]^{3+}$ (—·—·—).

Table 1. Absorption data of the complexes in aqueous solutions: $\nu_{max}$[a] (log $\varepsilon_{max}$)

| Complex | First band | Second band | Charge transfer band |
|---|---|---|---|
| $[Co(bgH)_3]^{3+}$ | 62.8 (2.30) | 84.8 (2.25) | 110.0 (3.56) |
| $[Co(bg)_3]$ | 62.2 (2.40) | *ca.* 84 (2.38) | *ca.* 102 (3.26) |
| $[Co(bg)_3]$[b] | 62.2 (2.38) | *ca.* 84 (2.31) | *ca.* 103 (3.27) |
| $[Co(bgH)_2(en)]^{3+}$ | 62.5 (2.25) | 85.7 (2.19) | *ca.* 110 (3.37) |
| $[Co(bg)_2(en)]^{+}$[b] | 62.5 (2.30) | *ca.* 85 (2.40) | *ca.* 102 (3.14) |
| $[Co(bgH)(en)_2]^{3+}$ | 61.2 (2.21) | 84.5 (2.11) | *ca.* 116 (3.50) |
| $[Co(bg)(en)_2]^{2+}$[b] | 58.8 (2.27) | 83.3 (2.25) | *ca.* 103 (3.04) |
| $[Co(guH)(en)_2]^{3+}$ | 61.8 (2.21) | *ca.* 78 (1.72)<br>87.0 (1.93) | *ca.* 115 (3.34) |
| $[Co(gu)(en)_2]^{2+}$[b] | 60.8 (2.26) | *ca.* 79 (1.82)<br>*ca.* 86 (2.06) | *ca.* 106 (2.98) |
| $[Co(en)_3]^{3+}$ | 64.0 (1.94) | 88.8 (1.90) | |

a) In the unit of $10^{13}$ sec$^{-1}$.

b) Measured in NaOH aqueous solutions using the corresponding bgH or guH complex.

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[13] S. F. Mason, *Inorg. Chim. Acta Rev.*, **2**, 89 (1968).

[14] B. Bosnich, *Accounts Chem. Res.*, **2**, 266 (1969); *Inorg. Chem.*, **7**, 2379 (1968).

[15] J. Ferguson, C. J. Hawkins, N. A. P. Kane-Maguire, and H. Lip, *Inorg. Chem.*, **8**, 771 (1969).

TABLE 2. CD DATA OF THE COMPLEXES IN AQUEOUS SOLUTIONS: $\nu_{ext}$[a] $(\varepsilon_l - \varepsilon_d)$

| Complex | First band | Second band | Charge transfer band | Ligand band |
|---|---|---|---|---|
| $(-)_{589}$-$[Co(bgH)_3]^{3+}$ | 58.8 (−3.52) | 83.3 (−1.84) | 100.0 (+0.75) | 123.5 (−44) |
| | 66.2 (+4.76) | | | 137.6 (+51) |
| $(-)_{589}$-$[Co(bg)_3]$[b] | 57.4 (−3.11) | 82.9 (−3.19) | | 114.5 (−36) |
| | 64.9 (+8.03) | | | 137.6 (+81) |
| $(+)_{589}$-$[Co(bgH)_2(en)]^{3+}$ | 56.2 (−0.70) | 83.8 (−1.09) | | 125 (−26.2) |
| | 64.9 (+4.73) | | | |
| $(+)_{589}$-$[Co(bg)_2(en)]^{+}$ [b] | 55.3 (−1.66) | 84.5 (−2.62) | | 117.6 (−36) |
| | 64.1 (+7.97) | | | 132.7 (+17.3) |
| $(+)_{589}$-$[Co(bgH)(en)_2]^{3+}$ | 61.6 (+3.24) | 84.5 (−0.48) | | |
| $(+)_{589}$-$[Co(bg)(en)_2]^{2+}$ [b] | 60.7 (+4.18) | 82.2 (−1.28) | | 120.0 (− 6.8) |
| $(+)_{589}$-$[Co(guH)(en)_2]^{3+}$ | *ca.* 59 (+2.0) | *ca.* 78 (−0.16) | | |
| | *ca.* 65 (+1.6) | 85.5 (−0.59) | | |
| $(+)_{589}$-$[Co(gu)(en)_2]^{2+}$ [b] | 59.8 (+3.40) | *ca.* 77 (−0.25) | | |
| | | 84.4 (−0.93) | | |
| $(+)_{589}$-$[Co(en)_3]^{3+}$ | 61.5 (+1.90) | 85.7 (+0.26) | | |
| | 70.6 (−0.14) | | | |

a) In the unit of $10^3$ sec$^{-1}$.
b) Measured in NaOH aqueous solutions using the corresponding bgH or guH complex.

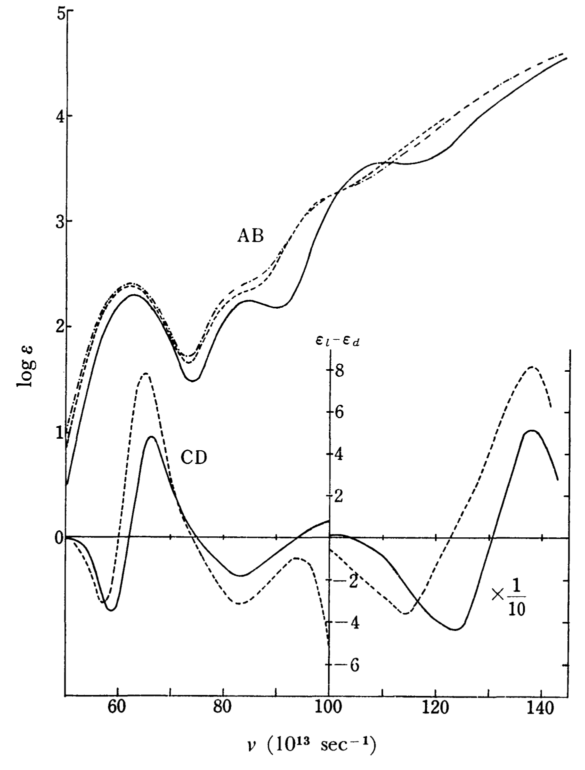

Fig. 2. Absorption (AB) and CD curves of (a) $(-)_{589}$-$[Co(bgH)_3]^{3+}$ and (b) $[Co(bg)_3]$: (a) in water (——), (a) in 0.10 N NaOH aq. soln. (----), and (b) in water (—·—·—).

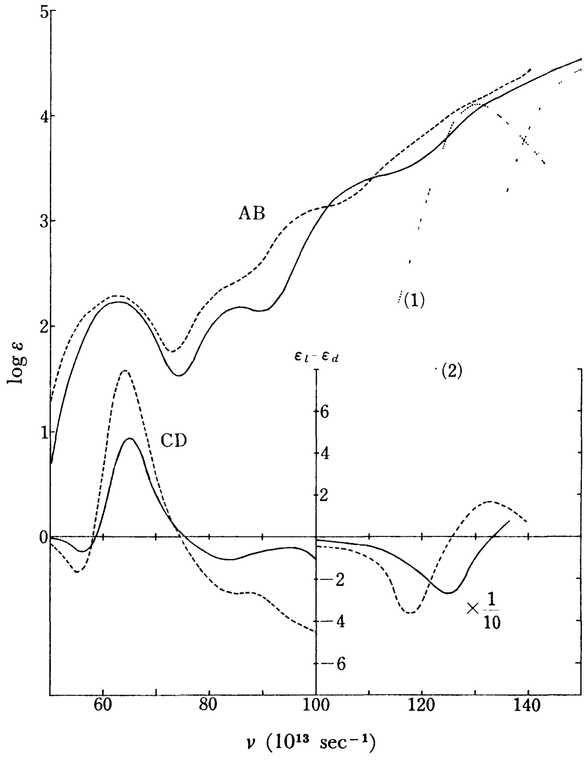

Fig. 3. Absorption (AB) and CD curves of $(+)_{589}$-$[Co(bgH)_2(en)]^{3+}$: in water (——) and in 0.25 N NaOH aq. soln. (----); and AB of biguanide sulfate monohydrate ($bgH \cdot H_2SO_4 \cdot H_2O$): in 0.10 N NaOH aq. soln. (1) (······) and in 0.10 N $H_2SO_4$ aq. soln. (2) (······).

which locate at about 270 mμ are not so contributed to CD that these bands may be considered to be charge transfer ones (or other kinds of inter ligand absorption bands).

The CD and absorption curves in NaOH aqueous solutions shift to the longer wavelength side on the whole than those in water, especially the bands which locate at the shorter wavelengths shift remarkably as seen in Figs. 2, 3, and 4. A similar red shift was also observed for the absorption curve of the free ligand biguanide (Fig. 3). The absorption curve of $(-)_{589}$-$[Co(bgH)_3]^{3+}$ in NaOH aqueous solution coincides well with that of $[Co(bg)_3]$ in water (Fig. 2). This fact points out that in 0.10 N NaOH aqueous solution, each of the three ligands of $(-)_{589}$-$[Co(bgH)_3]^{3+}$ is deprotonated and consequently $(-)_{589}$-$[Co(bgH)_3]^{3+}$ changes to optically active $[Co(bg)_3]$. It may be suggested that in the

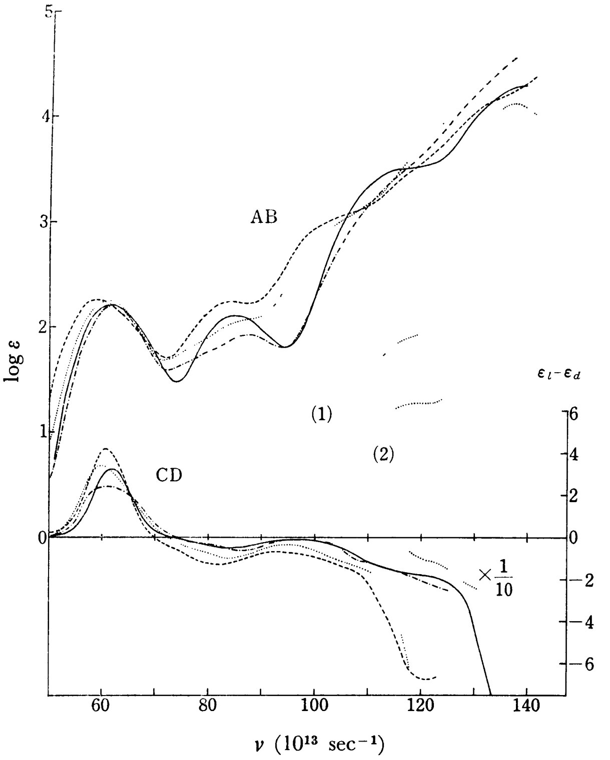

Fig. 4. Absorption (AB) and CD curves of (a) $(+)_{589}$-$[Co(bgH)(en)_2]^{3+}$ and (b) $(+)_{589}$-$[Co(guH)(en)_2]^{3+}$: (a) in water (——), (a) in 0.25 N NaOH aq. soln. (----), (b) in water (—·—·—), and (b) in 0.25 N NaOH aq. soln. (······); and AB of guanylurea sulfate dihydrate ($(guH)_2\cdot H_2SO_4\cdot 2H_2O$): in 0.10 N NaOH aq. soln. (1) (······) and in 0.10 N $H_2SO_4$ aq. soln. (2) (······).

cases of $(+)_{589}$-$[Co(bgH)(en)_2]^{3+}$ and $(+)_{589}$-$[Co(bgH)_2(en)]^{3+}$ also the corresponding optically active bg$^-$ complexes are formed in the alkaline solutions. Shift or intensification of the CD bands by such deprotonation occurred in the d-d absorption band region and these are also the case of the addition of sodium phosphate or selenite; then it was impossible to use the socalled "ion-paring criterion" proposed by Mason *et al.*,[16] for the component assignment of these biguanide complexes. Thus the assignment proposed by Brubaker and Webb[6] for the CD components of the first absorption band of $(-)_{589}$-$[Cr(bgH)_3]^{3+}$ from this criterion may be meaningless.

2. *The Characterization of the Guanylurea Complex.* As described in Experimental section, the analytical results suggest that the complex which was derived from $[Co(Cl)_2(en)_2]Cl$ and biguanide is $[Co(bgH)(en)_2]^{3+}$ and that the one from $[Co(CO_3)(en)_2]Cl$ and biguanide sulfate is $[Co(guH)(en)_2]^{3+}$. In the latter case, the biguanide is hydrolyzed into the guanylurea in the course of the reaction with $[Co(CO_3)(en)_2]Cl$.

The first absorption band of $[Co(guH)(en)_2]^{3+}$ is similar to that of $[Co(bgH)(en)_2]^{3+}$ as is shown in Fig. 4. Considering the fact that the effective symmetry of the former is much lower than that of the latter, it is expected that the first band of the former splits into two or more components. This consideration is realized in the CD spectra; namely, $[Co(guH)(en)_2]^{3+}$ exhibits an overlapped pattern of two positive CD bands, whereas $[Co(bgH)(en)_2]^{3+}$ shows only one positive (Fig. 4). Contrary to the first absorption band region, the second absorption band of $[Co(guH),(en)_2]^{3+}$ differs remarkably from that of $[Co(bgH)(en)_2]^{3+}$. The second band of the former splits into two components at 345 mμ and *ca.* 385 mμ, though the CD spectra of both the complexes are similar to one another in the corresponding region. It should be noted that the guanylurea complex is a rather rare example which shows the apparent splitting in the second absorption band. The CD and absorption curves shift to the longer wavelengths in alkaline solutions than those in water, especially in the region of the ultraviolet ligand absorption band; the absorption curve of the free ligand also shift to red in alkaline solution.

From the data presented in Table 1, it has been concluded that the spectrochemical series of the ligands concerned in this paper is

$$\text{en} > \text{guH} > \text{bgH} > \text{gu}^- > \text{bg}^-.$$

It is unknown which of the O and N atoms of the urea part in the guanylurea ligand is coordinated to the central cobalt(III) ion. This is also the case of a tris-guanylurea complex of cobalt(III).[2]

3. *Absolute Configuration.* Currently there have been encountered some difficulties in the attempt to make an inference of the absolute configuration of a tris-chelate type cobalt(III) or chromium(III) complex from the comparison of its CD signs in the region of the *d-d* or the ultraviolet ligand absorption bands to those of a reference complex, whose absolute configuration has been determined conclusively.

It is well known that MaCaffery and Mason[17] assigned a strong positive CD component at 61.5 ($10^{13}$ sec$^{-1}$) of $(+)_{589}$-$[Co(en)_3]^{3+}$, whose absolute configuration was unequivocally determined by an X-ray technique by Saito *et al.*[8,18,19] to the transition $^1A_1$-$^1E_a$ of the first absorption band from the CD measurement of a single crystal of $Na(+)_{589}$-$[Co(en)_3]_2Cl_7\cdot 6H_2O$; therefore another weak negative CD component at 70.6 ($10^{13}$ sec$^{-1}$) of this complex should be assigned to a $^1A_1$-$^1A_2$ or to any other origin. Recently, Judkins and Royer[20] measured the single crystal CD spectra of $\Delta(+)_{589}$-$[Co(tn)_3]Cl_3\cdot 4H_2O$ containing trimethylenediamine (tn), whose absolute configuration was determined by Nomura *et al.*,[21] and reported that the relative positions of the $A_2$ and $E_a$ components are reversed in this complex as compared with those found in $[Co(en)_3]^{3+}$; this means the $E_a$ and the $A_2$ components of the $\Delta$ isomer of trimethylenediamine complex have positive and negative signs, respectively. Jud-

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kins and Royer explained this contradiction between the ethylenediamine and trimethylenediamine complexes on the line of Piper's prediction[22,23] that stated, if the N-M-N angle in the chelate ring, $\alpha$, is greater than 90°, the sign of the Cotton effects will reverse with respect to the complex with $\alpha$ less than 90°; the angle $\alpha$ of the $[\mathrm{Co(en)_3}]^{3+}$ and $[\mathrm{Co(tn)_3}]^{3+}$ have been reported to be 87.4°[19] and 94.5°,[21] respectively.

Unfortunately, Brubaker, and Webb reported that all three angles $\alpha$ of $[\mathrm{Cr(bgH)_3}]^{3+}$ are 90° within experimental error, though this is for a chromium(III) and not for the cobalt(III) complex. In the meanwhile, the $\Lambda(-)_{589}$-$[\mathrm{Cr(bgH)_3}]^{3+}$ has almost identical CD pattern in the *d-d* absorption band region to that of the $(-)_{589}$-$[\mathrm{Co(bgH)_3}]^{3+}$. Accordingly, as far as we concern the *d-d* absorption band region, the $(-)_{589}$-$[\mathrm{Co(bgH)_3}]^{3+}$ may be assigned to have the absolute configuration $\Lambda$, and the correspondency which is seen in Fig. 1 may suggest that all the isomers presented in Fig. 1 have the same absolute configuration $\Lambda$. Nevertheless, a serious difficulty comes from the ultraviolet CD spectra as mentioned in Section 1 above; the criterion from the so-called exciton splitting shows reverse assignment, $\Delta$, at least for the $(-)_{589}$-$[\mathrm{Co(bgH)_3}]^{3+}$ and $(+)_{589}$-$[\mathrm{Co(bgH)_2(en)}]^{3+}$ and their deprotonated species. A similar case has been found for $[\mathrm{Co(dip)_3}]^{3+}$ (dip=2,2′-dipyridyl); the $(-)_{589}$ isomer has positive sign in the main CD component of the first absorption band and the negative and positive exciton splitting CD components, at longer and shorter wavelengths respectively, in the ultraviolet ligand absorption band region.[15] Clearly further studies are needed for these anomalies.

The overlapped positive CD components of the $(+)_{589}$-$[\mathrm{Co(guH)(en)_2}]^{3+}$ in the first absorption band region suggest that this $(+)_{589}$ isomer has an absolute configuration $\Lambda$. It may be noticed that all the isomers containing biguanide or guanylurea, which were suggested to have absolute configuration $\Lambda$ from the behavior in the first absorption band, have commonly negative CD bands in the second absorption band region.

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