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# Preparation of *cis*- and *trans*-Dicyanobis(ethylenediamine)chromium(III) Complexes and Optical Resolution of the *cis* Isomer

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Two geometrical isomers, *cis* and *trans*, of $[Cr(CN)_2(en)_2]^+$ were prepared and the *cis* isomer was resolved into optical isomers. The ligand field absorption and circular dichroism spectra were discussed and the absolute configuration of *cis*-$(+)_{546}$-$[Cr(CN)_2(en)_2]^+$ was determined to $\Lambda$ on the basis of the circular dichroism sign in the first spin-allowed d-d band region.

There has been known only one series, though incomplete, of mixed cyano chromium(III) complexes, *i.e.*, aquacyano complexes, $[Cr(CN)_n(OH_2)_{6-n}]^{3-n}$,[1-2] which have been studied in solution, but not isolated as solid complexes. No mixed cyanoamine or cyanoammine chromium(III) complexes have been known.

In the present paper, the preparation and characterization of an isomeric pair of dicyanobis(ethylenediamine)chromium(III) perchlorate or chloride, *cis*- and *trans*-$[Cr(CN)_2(en)_2]X$, and the optical resolution of the *cis* isomer will be reported. Their infrared and visible absorption and circular dichroism (CD) spectra will be discussed in connection with the other dianionobis(ethylenediamine)chromium(III) complexes and in comparison with the corresponding mixed cyano cobalt(III) complexes.

## Experimental

*Preparation of* cis- *and* trans-*Dicyanobis(ethylenediamine) chromium (III) Complexes.* Twenty grams of $[Cr(en)_3]Cl_3\cdot 3.5H_2O$ and 4.8 g of NaCN were dissolved in 80 ml of water and to this solution was added 2 g of activated charcoal. The mixture was kept with stirring at room temperature for a week. After removing the activated charcoal, a yellow compound (*ca.* 6 g) was deposited by adding methanol and acetone to the filtrate. This was filtered off, because the yellow compound was confirmed to be the unreacted complex, $[Cr(en)_3]Cl_3$, by absorption measurement. The filtrate was condensed by a vacuum rotatory evaporator. Then about 4 g of another yellow precipitate was obtained by adding acetone. This yellow compound showed an absorption band at 438 nm. The aqueous solution of the product was poured into a column (300×20 mm) of a strong-acid cation-exchange resin (Dowex 50 W×8, 200—400 mesh, lithium form), and the column was swept with water. When the adsorbed band was eluted with 0.5 M aqueous solution of lithium perchlorate, two yellow bands were eluted. From the first eluate, yellow leaflet crystals were obtained by condensing and cooling. The second eluate was concentrated by a vacuum rotatory evaporator. To the condensed solution was added acetone–methanol mixture. Then yellow powder was obtained. The yield was about 1 g for the first eluate and about 2 g for the second eluate. The product from the second eluate (isomer II) was found to be more soluble than the one from the first eluate (isomer I). These complexes were recrystallized from warm water–methanol mixture. Found for the isomer I (*trans* form): C, 22.64; H, 5.06; N, 25.81%. Found for the isomer II (*cis* form): C, 22.01; H, 5.19; N, 25.48%. Calcd for $[Cr(CN)_2(en)_2]ClO_4$: C, 22.27; H, 4.98; N, 25.96%. In order to obtain more soluble complex salts, the perchlorates were converted to chlorides by using an anion-exchange resin of chloride form. The chlorides of isomer I and II were found to be anhydrous and monohydrated, respectively, from the elemental analyses. Found for the isomer I: C, 27.34; H, 6.28; N, 32.01%. Calcd for $[Cr(CN)_2(en)_2]Cl$: C, 27.75; H, 6.21; N, 32.36%. Found for the isomer II: C, 26.19; H, 6.30: N, 30.69%. Calcd for $[Cr(CN)_2(en)_2]Cl\cdot H_2O$: C, 25.95; H, 6.53; N, 30.26%.

*Optical Resolution of the Isomer II.* The chloride of isomer II, $[Cr(CN)_2(en)_2]Cl\cdot H_2O$ (0.544 g, 0.002 mol) was dissolved in 5 ml of warm water. To this solution was added $(+)_{589}$-ammonium $\alpha$-bromocamphor-$\pi$-sulfonate ($NH_4\cdot$*d*-BCS) (0.328 g, 0.001 mol) in 5 ml of water. Then yellow crystals of the least soluble diastereomer were precipitated. The yield was about 0.4 g. $[\alpha]_{546}=+94.7°$, $[\alpha]_{589}=+66.8°$. Found: C, 35.90; H, 5.68; N, 15.70%. Calcd for $[Cr(CN)_2(en)_2]\cdot$*d*-BCS: C, 35.96; H, 5.66; N, 15.73%. The diastereomer was converted to the perchlorate and chloride by the following procedure. The *d*-BCS salt was suspended in a small amount of cold 70% $HClO_4$, and then the perchlorate was deposited by the addition of cold methanol. $[M]_{546}=+19°$. Found: C, 22.09; H, 5.02; N, 25.75%. Calcd for $(+)_{546}$-$[Cr(CN)_2(en)_2]ClO_4$; C, 22.27; H, 4.98; N, 25.96%. The *d*-BCS salt was converted to the chloride by using an anion exchange resin of chloride form. The crude complex obtained was recrystallized from water–ethanol. Found: C, 26.70; H, 6.57; N, 31.01%. Calcd for $(+)_{546}$-$[Cr(CN)_2(en)_2]Cl\cdot 0.5H_2O$: C, 26.83; H, 6.38; N, 31.28%.

*Measurements.* The visible absorption spectra were obtained with a Shimadzu UV-200 spectrophotometer. The CD spectra were recorded on a Jasco MOE-1 spectropolarimeter. A Yanagimoto spectropolarimeter, Model 185, was used to check optical rotatory power. The infrared spectra in the region of 4000—600 $cm^{-1}$ were measured with a Jasco DS-402G spectrophotometer. The far-infrared spectra in the region of 700—200 $cm^{-1}$ were obtained by a Hitachi FIR-3 far-infrared spectrophotometer.

## Results and Discussion

*a) The Preparative Method.* In general, the syntheses of dianionobis(ethylenediamine)chromium(III) complexes, especially, of the *trans* forms, are rather difficult. Among the known methods a relatively efficient and convenient one is the thermal decomposition of $[Cr(en)_3]X_3$, which yields $[CrX_2(en)_2]X$.[3] O'Brien and Bailar[4] attempted the thermal decomposition of $[Cr(en)_3](CN)_3$, but failed in obtaining $[Cr(CN)_2(en)_2]CN$. Recently the progress has been made of the syntheses of mixed cyano-ammine or -amine complexes of cobalt(III) by four or more methods.[5-8] In the present work, two of them were applied to the chromium(III) analogues. One is based on the reaction of *cis*- or *trans*-$[CoCl_2(en)_2]Cl$ with NaCN in dimethyl sufoxide,[5] and the other on the reaction of $[Co(en)_3]Cl_3$ with NaCN in an aqueous solution in the presence of activated charcoal.[6] By the application of the latter method $[Cr(CN)_2(en)_2]^+$ was successfully prepared, whereas the application of the former method was unsuccessful. The formation of *cis*-$[Cr(CN)_2(en)_2]Cl\cdot H_2O$, however, was confirmed by Matsumoto *et al.*[9] from the reaction of $[Cr(en)_3]Cl_3$ and NaCN in dimethyl sulfoxide. In the present method, the yield of *cis*-$[Cr(CN)_2(en)_2]^+$ was about twice as high as that of *trans* one. The abundance of *cis* isomer was also found in the corresponding cobalt(III) complexes.[6]

*b) Identification.* The two isomers isolated in this work have the same chemical composition, but exhibit differences in their solubilities, elution behaviors on cation-exchange column chromatography and crystalline forms.

Although the geometrical isomers of most dianionobis(ethylenediamine) complexes can be distinguished from each other by the spectral behavior in the first absorption band region, the present complexes give quite similar absorption spectra (but with different intensities as in Fig. 1 and Table 1) as in the case of *cis*- and *trans*-$[Cr(NCS)_2(en)_2]^+$.[10] That is, there is no clue for the assignment of geometrical configurations in the absorption spectra. However, since the second eluate (isomer II) was resolved into the enantiomers through its $(+)_{589}$-α-bromocamphor-π-sulfonate, this isomer is the *cis* form, and consequently the first eluate (isomer I) is to be assigned to the *trans* form.

TABLE 1. ABSORPTION (AB) AND CD DATA FOR CHROMIUM(III) COMPLEXES IN THE d–d TRANSITIONS
(Wave numbers are in $10^3$ $cm^{-1}$)

| AB ($\log \varepsilon_{max}$) | CD ($\Delta\varepsilon_{ext}$) |
|---|---|
| *cis*-$[Cr(CN)_2(en)_2]^+$ | *cis*-$(+)_{546}$-$[Cr(CN)_2(en)_2]^+$ |
| 14.24 ($\bar{1}$.41) | 14.51 ($+6.5\times10^{-4}$) |
| 14.63 ($\bar{1}$.39) | 14.75 ($-7.2\times10^{-4}$) |
| 15.02 ($\bar{1}$.43) | |
| 23.10 (1.85) | 23.33 (+0.51) |
| 29.48 (1.80) | 29.85 (−0.036) |
| *trans*-$[Cr(CN)_2(en)_2]^+$ | |
| 23.15 (1.69) | |
| 29.67 (1.63) | |

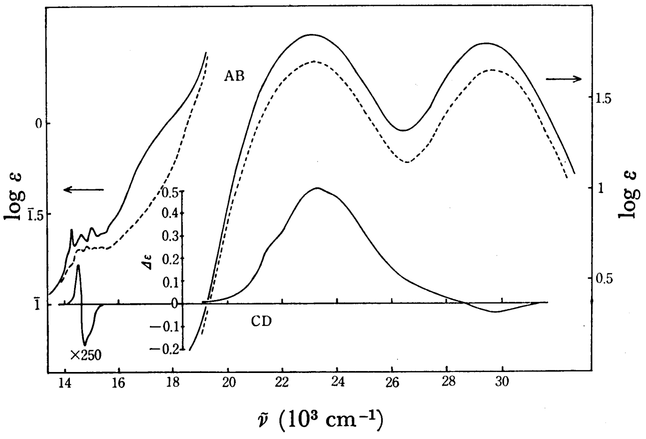

Fig. 1. Absorption curves of *cis*- (——) and *trans*-$[Cr(CN)_2(en)_2]^+$ (----), in water. CD curve of *cis*-$(+)_{546}$-$[Cr(CN)_2(en)_2]^+$ (——) in water.

It is generally found that *cis*-dianionobis(ethylenediamine)chromium(III) perchlorate is more soluble than the *trans* one.[11] This is also the case for the present complexes. The column chromatographic elution order also agrees with that generally recognized for *cis*- and *trans*-isomers of bis(ethylenediamine) type complexes.[6,12]

The infrared absorption spectrum of the *trans* isomer exhibits a simpler pattern than that of the *cis* one in the region of 4000—200 $cm^{-1}$, as in the case of the similar type chromium(III) and cobalt(III) complexes.[13] Particularly, the $NH_2$ bending near 1600 $cm^{-1}$ and the $CH_2$ rocking bands at 800—900 $cm^{-1}$ can discriminate between two geometrical isomers of dianionobis(ethylenediamine) complexes. In the isomer II, the former bands are observed at 1582 and 1605 $cm^{-1}$ and the latter at 860 and 880 $cm^{-1}$, while in the isomer I only one component at 1600 $cm^{-1}$ and undefinitely split ones at about 880 $cm^{-1}$. Hughes *et al.*[14] measured the far-infrared spectra of various kinds of bis(ethylenediamine) chromium(III) complexes, and found that there is a compatible difference between the spectra of *cis* and *trans* isomers in the region of 550—395 $cm^{-1}$, where the δ-Cr–N+ring deformation may occur. In fact, four bands are observed for *cis*-$[Cr(CN)_2(en)_2]Cl\cdot H_2O$ in the corresponding region and three bands for the *trans* one. In the Cr–C and Cr–N stretching band region (360—220 $cm^{-1}$), the *cis* isomer shows more splitting components than the *trans* one as in the other bis(ethylenediamine) complexes.[14] All the facts of the infrared absorption spectra support the present assignment of geometrical configurations. While the corresponding cobalt(III) complexes, *cis*- and *trans*-$[Co(CN)_2(en)_2]^+$, give a strong and sharp CN stretching band near 2100 $cm^{-1}$,[6] the present chromium(III) complexes give very weak bands in this region. It has been revealed that the CN stretching band of $K_3[Cr(CN)_6]$ is about one-nineth as weak in intensity as $K_3[Co(CN)_6]$, probably owing to the difference in the M–CN π-bonding.[15] Thus, it seems plausible that the mixed cyano chromium(III) complexes also show this phenomenon.

*c) The Absorption and CD Spsctra.* The ligand field absorption spectra of *cis*- and *trans*-$[Cr(CN)_2(en)_2]^+$ are nearly identical with each other as mentioned in b). That is, the first and the second absorption bands of *cis*-$[Cr(CN)_2(en)_2]^+$ locate at 23.1 and 29.48 kK, respectively, while those of the *trans* isomer at 23.15 and 29.67 kK. The molar absorptivities of the *cis* isomer are larger than those of the *trans* isomer for both the first and second band region, as in Fig. 1 and Table 1. This intensity order coincides with the other cases found in literature for the *cis*- and *trans*-dianionobis(ethylenediamine) complexes, for example *cis*- and *trans*-$[Cr(NCS)_2(en)_2]^+$.[10]

The angular overlap model[16] or Yamatera's rule[17] predicts that the first excited quartet state ($^4T_{2g}$) in $O_h$

symmetry splits into the nondegenerate ($^4A_1$) component at 24.18 kK and the accidentally degenerate ($^4A_2$ and $^4B_2$) one at 23.01 kK for the *cis* isomer of $C_{2v}$ symmetry, while the *trans* isomer of $D_{4h}$ symmetry has the nondegenerate ($^4B_{2g}$) component at 21.85 kK and the degenerate ($^4E_g$) one at 24.18 kK. On the other hand, Perumareddi[18] has predicted from the ligand field theory the absorption maxima of *cis*- and *trans*-$[Cr(CN)_2(NH_3)_4]^+$, of which the ligand field parameters are very close to those of *cis*- and *trans*-$[Cr(CN)_2(en)_2]^+$; that is, *cis*-$[Cr(CN)_2(NH_3)_4]^+$ has two split components at 24.025 and 22.788 kK and the *trans* one at 23.802 and 21.550 kK. The theoretically predicted energy interval between the degenerate and the nondegenerate components in the first band region of the *trans* dicyano complex is about twice as large as that of the *cis* one and comparable to the splitting of *trans*-$[Cr(OH_2)_2(en)_2]^{3+}$, of which the first band has been reported to split largely.[10] The present *trans* complex, however, exhibits no splitting and its half-width is equal to that of the *cis* one. The absorption maxima of both the *trans*- and *cis*-complexes agree fairly well with the weighted mean value of the predicted components as in Table 2. A discrepancy between the theoretical prediction and observation has also been found for the corresponding *trans* dicyano cobalt(III) complexes.[6] The second absorption band maxima of both the present isomers are close to the value obtained from the weighted mean expression or the rule of the average environment.[19]

TABLE 2. THE PREDICTED POSITIONS OF THE FIRST ABSORPTION BAND IN UNIT OF $10^3$ $cm^{-1}$

| Ligand field theory[a] | | Yamatera's rule[b] | |
|---|---|---|---|
| *cis*-$[Cr(CN)_2(en)_2]^+$ | | | Weighted mean |
| $^4A_2$, $^4B_2$ | 22.788 | 23.01 | 23.40 |
| $^4A_1$ | 24.025 | 24.18 | |
| *trans*-$[Cr(CN)_2(en)_2]^+$ | | | |
| $^4B_{2g}$ | 21.550 | 21.85 | 23.40 |
| $^4E_g$ | 23.802 | 24.18 | |

a) The value of the tetraammine complexes after Perumareddi[18] b) Using the parameters, $\delta(en)=0$ and $\delta(CN)=10Dq(CN)-10Dq(en)=4.66$

The CD spectrum of $(+)_{546}$-$[Cr(CN)_2(en)_2]^+$ shows a positive band with an undefined inflection in the first absorption band region and a negative band in the second absorption band region as shown in Fig. 1 and Table 1. Since the positive CD band in the first absorption band region is due to the $^4E(^4T_{2g})$ parentage of the parent trigonal complex, the absolute configuration of this $(+)_{546}$-isomer is assigned to $\Lambda$.

In the near-infrared region around 14—15 kK, where the quartet-doublet spin-forbidden transitions occur, the narrow and sharp but weak absorption bands are observed as in Fig. 1. The absorption bands in this region for the *cis* and *trans* isomers differ in their patterns from each other. Three distinct peaks are observed for the *trans* isomer, while some uncertain structural inflections appear for the *cis* one. In the corresponding region, two CD peaks, (+) and (−) from the longer wavelength side, are observed for the *cis*-$(+)_{546}$-isomer. It is found that their CD intensities are about 0.1% of that in the first spin-allowed band region. Provided that the theoretical relationship between rotational strengths for the spin-forbidden and spin-allowed transitions, which has been presented recently for the trigonal chromium(III) complexes,[20] may be applicable also to the *cis*-dianionobis(ethylenediamine) complexes, the positive CD component at the longer wavelength side may be due to the $^2E \leftarrow {^4A_2}$ transition and the remaining negative one to the split component of the $^2T_1$, $\bar{E}_b$. Since the rotational strength for the spin-forbidden transitions is contributed from that for the spin-allowed transitions with same signs,[20] the intensity of negative CD component in the spin-forbidden band region should originate from the negative CD component in the first spin-allowed band region. Therefore, the CD in the first band region may consist of two components with opposite signs, and then it is supposed that a negative minor CD band may be destructively superimposed on the positive major CD band. On the other hand, for the corresponding cobalt(III) complex, $\Lambda(+)_{589}$-$[Co(CN)_2(en)_2]^+$, the CD spectra in the first band region give two positive components.[21] Accordingly, it is suggested that the CD behavior of the present chromium(III) complex differs considerably from that of the corresponding cobalt(III) complex, although current CD theories propose that the rotational strengths of low spin cobalt(III) complexes behave analogously to those of chromium(III) complexes.[22]

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