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Trimethylenediamine Complexes. VIII.[1] Some Cis-Trans Isomeric Pairs of the Bis(trimethylenediamine)chromium(III) Complexes

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The cis-trans isomeric pairs of diisothiocyanato-, dinitrito-, diazido-, diaqua-, and aquahydroxo-bis(trimethylenediamine)chromium(III) complexes have been obtained as crystals and characterized by infrared and electronic absorption spectra. The cis isomers of diisothiocyanato and diazido complexes as well as $[Cr(N_3)_2(en)_2]ClO_4$ were resolved and the absolute configurations of $(+)_{589}$-*cis*-$[Cr(NCS)_2(tn)_2]SCN$, $(+)_{589}$-*cis*-$[Cr(N_3)_2(tn)_2]ClO_4$, and $(-)_{589}$-*cis*-$[Cr(N_3)_2(en)_2]ClO_4$ were all assigned to Δ.

Comparative Chemistry of the five-membered ethylenediamine (en) chelates and the six-membered trimethylenediamine (tn) chelates is interesting from both the structural and kinetic viewpoints. Absolute configurations of several optically active cobalt(III) complexes containing trimethylenediamine as a ligand have been established by X-ray analysis,[2] and the empirical criterion of McCaffery *et al.*[3] relating the absolute configuration to the CD-spectral feature in the first d-d band region has been shown to hold in these complexes. On the other hand, optically active chromium(III) trimethylenediamine complexes are rather few, and only four examples, $(-)_{589}$-$[Cr(tn)_3]^{3+}$,[4] $(+)_{589}$-*cis*-$[CrCl_2(tn)_2]ClO_4$,[5] $(+)_{589}$-$[Cr(acac)(tn)_2]I_2\cdot 0.5H_2O$,[1] and $(-)_{589}$-$[Cr(acac)_2(tn)]I\cdot H_2O$[1] have been reported so far, and further development in this field is desirable.

The aquation rates of *trans*-$[CoCl_2(tn)_2]^+$ and *trans*-$[CoBr_2(tn)_2]^+$ are extraordinarily large as compared with those of the corresponding ethylenediamine complexes,[6] but *trans*-$[CrCl_2(tn)_2]^+$ hydrolyzes in acid solution with a rate comparable to that of *trans*-$[CrCl_2(en)_2]^+$.[7] The cis isomer of $[CoCl_2(tn)_2]^+$ is unknown,[8] although *cis*-$[CoCl_2(en)_2]^+$ is easily prepared by heating the trans isomer in aqueous solution. On the other hand, *cis*-$[CrCl_2(tn)_2]ClO_4\cdot 0.5\,H_2O$ was obtained as violet crystals, although it is liable to isomerize to the *trans* form in solution.[5] Thus further comparison of the thermodynamic and kinetic ring-size effects in the chromium(III) and cobalt(III) complexes may be interesting.

In previous papers we have prepared and characterized several cis-trans isomeric pairs of dianionbis(trimethylenediamine)cobalt(III) complexes,[9] and compared the ligand substitution rates of some trimethylenediamine cobalt(III) complexes with those of the corresponding ethylenediamine complexes.[10] The present paper reports preparation and characterization of some bis(trimethylenediamine)chromium(III) complexes inclusive of the optically active *cis*-$[Cr(NCS)_2(tn)_2]^+$ and *cis*-$[Cr(N_3)_2(tn)_2]^+$ complexes.

Experimental

Preparation and Optical Resolution of Complexes. The starting compounds, *cis*-$[CrCl_2(tn)_2]Cl\cdot H_2O$ and *trans*-$[CrCl_2(tn)_2]Cl$ were prepared by the method of Pedersen.[5] Commercially available potassium antimony(III) (*R,R*)-tartrate was used without further purification. Another resolving agent, (*R,R*)-di-*O*-benzoyltartaric acid was prepared by the reaction between (*R,R*)-tartaric acid and benzoyl chloride[11] and used after partial neutralization with one-half equivalent of sodium hydroxide.

cis-*Diisothiocyanatobis(trimethylenediamine)chromium(III) Thiocyanate Hydrate,* cis-$[Cr(NCS)_2(tn)_2]SCN\cdot H_2O$: Aqueous solution (10 ml) of *cis*-$[CrCl_2(tn)_2]Cl\cdot H_2O$ (1.1 g) was heated at 70 °C on a water-bath for 10 min to result in a red-orange solution, to which was added sodium thiocyanate (1.6 g) and heating was continued for about 1 h to obtain an orange precipitate. After cooling to room temperature, another portion (1.0 g) of sodium thiocyanate was added to the mixture, which was then allowed to stand overnight. The crude product was filtered, washed with cold water and air-dried. The yield was 1.2 g (92.6%). Recrystallization from hot water gave orange needles.

trans-*Diisothiocyanatobis(trimethylenediamine)chromium(III) Thiocyanate,* trans-$[Cr(NCS)_2(tn)_2]SCN$: The reaction of *trans*-$[CrCl_2(tn)_2]Cl$ (1.0 g) with sodium thiocyanate was performed in a similar manner as above to obtain orange crystals in an 80.9% (1.0 g) yield. Recrystallization from hot water gave orange plates.

cis-*Diaquabis(trimethylenediamine)chromium(III) Nitrate,* cis-$[Cr(H_2O)_2(tn)_2](NO_3)_3$: A solution (5 ml) of silver nitrate (1.7 g) was added to an aqueous solution (10 ml) of *cis*-$[CrCl_2(tn)_2]Cl\cdot H_2O$ (1.1 g) and the mixture was stirred at room temperature for 1 h to complete the reaction. A precipitate of silver chloride was filtered. Concentrated nitric acid (20 ml) and ethanol (50 ml) were added to the combined washings and the solution was left in a refrigerator to deposit an orange precipitate in a 69.8% (1.0 g) yield. The crude product was dissolved in a minimum amount of water and a few drops of concentrated nitric acid was added to the solution. On cooling in ice orange plate precipitated.

cis-*Aquahydroxobis(trimethylenediamine)chromium(III) Nitrate Hemihydrate,* cis-$[CrOH(H_2O)(tn)_2](NO_3)_2\cdot 0.5H_2O$: To an aqueous solution (5 ml) of *cis*-$[Cr(H_2O)_2(tn)_2](NO_3)_3$ (1.0 g) was added aqueous ammonia drop by drop to adjust pH to *ca.* 7, color of the solution changing from orange to red. Ethanol (50 ml) was poured into the solution to deposit a red precipitate. The yield was 0.8 g (94.0%). Recrystallization from water–ethanol gave red needles which are slightly hygroscopic.

trans-*Aquahydroxobis(trimethylenediamine)chromium(III) Nitrate,* trans-$[CrOH(H_2O)(tn)_2](NO_3)_2$: One gram of *trans*-$[CrCl_2(tn)_2]Cl$ was dissolved in hot water. A solution (5 ml) of silver nitrate (1.7 g) was added and the mixture was kept at 50 °C for 2 h to complete the reaction. After cooling to room temperature, silver chloride was filtered. On addition of aqueous ammonia dropwise to the combined washings to attain pH≈7 (solution turning red), red-brown thin crystals precipitated. The yield was 0.3 g (25.6%). After separation of the product, concentrated nitric acid (20 ml) and ethanol (50 ml) were added to the filtrate and the mixture was kept in a refrigerator to deposit an orange precipitate, which was identified as *cis*-$[Cr(H_2O)_2(tn)_2](NO_3)_3$ on the basis of IR and electronic spectra. The yield of the *cis*-diaqua complex was 0.6 g (43.6%).

trans-*Diaquabis(trimethylenediamine)chromium(III) Nitrate,* trans-$[Cr(H_2O)_2(tn)_2](NO_3)_3$: The aquahydroxo complex *trans*-$[CrOH(H_2O)(tn)_2](NO_3)_2$ (1.0 g) was dissolved in *ca.* 8 M nitric acid (20 ml) and the solution was stirred for a while to separate out a red-brown precipitate in an 85.1% (1.1 g) yield. The crude product was dissolved in a minimum amount of water. After filtration, the solution was kept in ice and concentrated nitric acid was added dropwise to it to precipitate red-brown needles.

cis-*Dinitritobis(trimethylenediamine)chromium(III) Perchlorate,* cis-$[Cr(ONO)_2(tn)_2]ClO_4$: Sodium nitrite (0.5 g) was added to an aqueous solution (10 ml) of *cis*-$[Cr(H_2O)_2(tn)_2](NO_3)_3$ (1.0 g) and the mixture was stirred for 10 min in an ice bath. After filtration, sodium perchlorate (2.0 g) was added to the filtrate and the solution was kept overnight in a refrigerator to deposit orange prisms. The yield was 0.74 g (79.8%). The product is slightly hygroscopic and was recrystallized from hot water. The compound is not so stable against light, but changes slightly to red on long standing.

trans-*Dinitritobis(trimethylenediamine)chromium(III) Perchlorate,* trans-$[Cr(ONO)_2(tn)_2]ClO_4$: The reaction of *trans*-$[Cr(H_2O)_2(tn)_2](NO_3)_3$ (1.0 g) with sodium nitrite (0.5 g) was performed in the same manner as above to obtain orange crystals of the trans isomer in a 91.6% (0.85 g) yield. Orange plates were obtained by recrystallization from hot water.

cis-*Diazidobis(trimethylenediamine)chromium(III) Perchlorate,* cis-$[Cr(N_3)_2(tn)_2]ClO_4$: An excess amount (15.0 g) of sodium azide was added to a solution of *cis*-$[Cr(H_2O)_2(tn)_2](NO_3)_3$ (15.0 g) in a mixture of acetic acid (10 ml) and water (30 ml) and the solution was heated at 50 °C for 10 min to turn deep violet. Sodium perchlorate (5.0 g) was added after cooling to room temperature and the mixture was kept in a refrigerator overnight to precipitate red plates. The yield was 4.8 g (35.2%). Recrystallization from acetone–ethanol gave red needles.

trans-*Diazidobis(trimethylenediamine)chromium(III) Perchlorate,* trans-$[Cr(N_3)_2(tn)_2]ClO_4$: Sodium azide (1.0 g) was added to an aqueous solution (10 ml) of *trans*-$[Cr(H_2O)_2(tn)_2](NO_3)_3$ (1.0 g) and the mixture was heated at 50 °C for 5 min to afford a red solution, to which was added sodium perchlorate (2.0 g) and heated at 50 °C for further 1.5 h to turn violet. After cooling to room temperature, 60% perchloric acid was added to adjust pH to *ca.* 7 and the solution was kept in a refrigerator overnight to deposit violet needles. The yield was 0.2 g (22.0%). Recrystallization from hot water gave deep violet plates.

Caution: Synthesis of the azido complexes must be performed in a good hood, since gaseous hydrazoic acid is evolved.

*$(+)_{589}$-*cis-*Diisothiocyanatobis(trimethylenediamine)chromium(III) Thiocyanate,* $(+)_{589}$-cis-$[Cr(NCS)_2(tn)_2]SCN$: A solution (100 ml) of sodium hydrogen (*R*,*R*)-di-*O*-benzoyltartrate (1.2 g) was added slowly to an aqueous solution (100 ml) of *cis*-$[Cr(NCS)_2(tn)_2]SCN\cdot H_2O$ (1.2 g) with stirring at 50 °C. After cooling to room temperature, a pink precipitate was filtered, washed with water and air-dried. The yield was 0.8 g. Found: C, 44.90; H, 4.94; N, 11.95%. Calcd for $[Cr(NCS)_2(tn)_2][HC_{18}H_{12}O_8]\cdot H_2O = C_{26}H_{35}N_6O_9S_2Cr$: C, 45.14; H, 5.16; N, 12.14%. The diastereoisomer (0.8 g) was dissolved in a solution (10 ml) of sodium thiocyanate (2.0 g) and sodium hydroxide (0.1 g), and the mixture was stirred in an ice bath for 5 min. An orange precipitate was filtered, washed with water and air-dried. The yield was 0.4 g. Recrystallization from acetone–diethyl ether gave orange needles. In order to assure the optical purity, the resolution process was repeated. Molar rotations in methanol are $[M]_{589} = +312°$ and $[M]_{436} = +937°$.

*$(-)_{589}$-*cis-*Diisothiocyanatobis(trimethylenediamine)chromium (III) Thiocyanate,* $(-)_{589}$-cis-$[Cr(NCS)_2(tn)_2]SCN$: A solution (50 ml) of potassium antimony (*R*,*R*)-tartrate (0.8 g) was added to a solution of *cis*-$[Cr(NCS)_2(tn)_2]SCN\cdot H_2O$ (1.0 g) in a mixture of acetone (40 ml) and water (40 ml), and the solution was left standing in a refrigerator for two days. Orange needles of diastereoisomer were filtered, washed with a small amount of cold water and air-dried. The yield was 0.6 g. Found: C, 23.31; H, 4.23; N, 13.11%. Calcd for $[Cr(NCS)_2(tn)_2]SbC_4H_2O_6\cdot 2H_2O = C_{12}H_{26}N_6O_8S_2SbCr$: C, 23.24; H, 4.23; N, 13.55%. The diastereoisomer was added to a solution (5 ml) of sodium thiocyanate (2.0 g) and the mixture was stirred for 10 min to deposit orange and white precipitates, which were filtered, washed with cold water and air-dried. Acetone dissolved the orange precipitate, leaving the insoluble white one. Diethyl ether was added to the combined washings to precipitate the $(-)_{589}$ isomer (0.3 g). The resolution procedure was repeated once again to assure the optical purity. The observed values of molar rotation in methanol, $[M]_{589} = -314°$ and $[M]_{436} = -936°$, show an excellent coincidence with those of the $(+)_{589}$ isomer which was obtained above by the resolution with sodium hydrogen-(*R*,*R*)-di-*O*-benzoyltartrate.

*$(+)_{589}$-*cis-*Diisothiocyanatobis(ethylenediamine)chromium(III) Thiocyanate,* $(+)_{589}$-cis-$[Cr(NCS)_2(en)_2]SCN$: This complex has already been resolved by House,[12] and both of pure $(+)_{589}$ and $(-)_{589}$ isomers were isolated in solution. Now for comparison with the corresponding trimethylenediamine complex, the ethylenediamine complex was resolved by potassium antimony (*R*,*R*)-tartrate and isolated as crystals of which the molar rotations are $[M]_{589} = +22°$, $[M]_{546} = +402°$ and $[M]_{436} = -704°$ in methanol and $[M]_{589} = +100°$, $[M]_{546} = -434°$ and $[M]_{436} = -810°$ in water.

*$(+)_{589}$-*cis-*Diazidobis(trimethylenediamine)chromium(III) Perchlorate,* $(+)_{589}$-cis-$[Cr(N_3)_2(tn)_2]ClO_4$: A solution (200 ml) of sodium hydrogen (*R*,*R*)-di-*O*-benzoyltartrate (4.8 g) was added slowly to an aqueous solution (250 ml) of the racemic complex (4.8 g). A red precipitate, which deposited from the solution kept in an ice bath for 1 h, was filtered, washed with cold water and air-dried. The yield was 2.7 g. Found: C, 44.08; H, 5.09; N, 21.16%. Calcd for $[Cr(N_3)_2(tn)_2][HC_{18}H_{12}O_8]\cdot H_2O = C_{24}H_{35}N_{10}O_9Cr$: C, 43.70; H, 5.35; N, 21.24%. A mixture of the diastereoisomer (0.9 g) and silver acetate (0.4 g) was stirred in water (10 ml) for 5 min. Acetone (50 ml) was added to the solution to precipitate the silver salt of resolving agent. Sodium perchlorate (2.0 g) was dissolved in the filtrate and acetone was distilled away under reduced pressure to deposit a red precipitate (0.35 g). Repeated resolution assured the optical purity of the product, of which the molar rotations are $[M]_{589} = +76°$ and $[M]_{436} = +1590°$ in water.

*$(-)_{589}$-*cis-*Diazidobis(ethylenediamine)chromium(III) Perchlorate,* $(-)_{589}$-cis-$[Cr(N_3)_2(en)_2]ClO_4$: Racemic *cis*-$[Cr(N_3)_2(en)_2]ClO_4$ (2.0 g) prepared according to the literature[13] was resolved by sodium hydrogen (*R*,*R*)-di-*O*-benzoyltartrate and worked up to obtain the optically active perchlorate as red-violet plates (0.3 g). Repeated resolution assured the optical purity. The molar rotations are $[M]_{589} = -754°$ and $[M]_{436} = +710°$ in water.

Measurements. The electronic absorption spectra were measured by a Hitachi EPS-3T spectrophotometer, and the IR spectra by JASCO IR-E (4000—600 cm^{-1}) and Hitachi

EPI-L (700—200 cm^{-1}) spectrometers. The optical rotations were determined with a Yanagimoto OR-50 polarimeter, and the CD spectra with a JASCO J-20 recording spectrometer.

Results and Discussion

Several kinds of cis-trans isomeric pairs of the bis(trimethylenediamine)chromium(III) complexes were prepared by the ligand substitution reactions of *cis*- and *trans*-$[CrCl_2(tn)_2]^+$ in aqueous solution. Results of the elemental analysis for the products are collected in Table 1. The ligand substitution reactions of these chromium(III) complexes proceeded with steric retention except in one case. As was described in Experiment, the yield of *trans*-$[CrOH(H_2O)(tn)_2](NO_3)_2$ from *trans*-$[CrCl_2(tn)_2]Cl$ was as low as 25.6% and acidification of the mother liquor gave *cis*-$[Cr(H_2O)_2(tn)_2](NO_3)_3$ in a 43.6% yield. Thus the hydrolysis of *trans*-$[CrCl_2(tn)_2]^+$ induced by the silver ion resulted in *ca.* 50% isomerization under the synthetic conditions. For the sake of comparison, the reaction of *trans*-$[CrCl_2(en)_2]^+$ with silver nitrate was examined, and only *trans*-$[Cr(H_2O)_2(en)_2]^+$ was obtained.

The spontaneous solvolysis of dihalogenobis(diamine)chromium(III) complexes usually occurs with essentially complete retention of configuration.[14] However the secondary hydrolysis of *trans*-$[CrCl_2(tn)_2]^+$ was reported to be complicated by isomerization.[7] The silver(I)-induced aquation of the $[CrCl_2(tn)_2]^+$ complexes seems to proceed *via* the **D** mechanism by analogy with the mercury(II)-catalyzed aquation of $[CrX(H_2O)_5]^{2+}$ (X= F, Cl, Br, and I).[15] It is noteworthy and deserves detailed investigation that the silver(I)-assisted complete aquation of *cis*-$[CrCl_2(tn)_2]^+$ occurs stereoretentively under the present synthetic conditions, while *trans*-$[CrCl_2(tn)_2]^+$ gives a mixture of *cis*- and *trans*-diaqua complexes.

The *cis*- and *trans*-dinitritobis(ethylenediamine)chromium(III) complexes have been synthesized and characterized by Garner and his coworkers.[16] Now the trimethylenediamine analogues are reported. When excess sodium nitrite was used, *cis*- and *trans*-$[Cr(ONO)_2(tn)_2]NO_2$ were obtained as hemihydrate and anhydrous salt, respectively. The cis nitrite salt is even more unstable than the perchlorate. Thus the crude product was obtained as lustrous brown plates, but lost lustre on washing with alcohol, decomposing rapidly. Optical resolution of the *cis*-$[Cr(ONO)_2tn_2]^+$ salts by means of sodium hydrogen (*R*,*R*)-di-*O*-benzoyltartrate was unsuccessful because of instability of the complex.

Wendlandt prepared *cis*-$[Cr(NCS)_2(tn)_2]SCN$ by the thermal matrix reaction.[17] In the present study the *cis*-diisothiocyanato complex was obtained as a hydrate by the reaction in aqueous solution, but changed curiously to anhydrous salts after optical resolution. Resolution of *cis*-$[Cr(NCS)_2(en)_2]^+$ was successful only by means of the antimony (*R*,*R*)-tartrate, and the values of molar rotation in aqueous solution nearly coincide with those reported by House.[12] Rotations in methanol were also recorded for comparison with $(+)_{589}$- and $(-)_{589}$-*cis*-$[Cr(NCS)_2(tn)_2]SCN$ whose solubilities in water are very poor.

Both *cis*- and *trans*-$[Cr(N_3)_2(tn)_2]ClO_4$ were obtained although *trans*-$[Cr(N_3)_2(en)_2]^+$ has not yet been reported. Both isomers are rather stable and can be recrystallized from hot water. The optical rotation of $(+)_{589}$-*cis*-$[Cr(N_3)_2(tn)_2]^+$ as well as that of $(+)_{589}$-*cis*-$[Cr(NCS)_2(tn)_2]^+$ shows no change after leaving for one day in aqueous solution at room temperature.

Infrared Spectra. Infrared spectra of the dianionobis(diamine)metal complexes are useful for distinguishing linkage[18] and geometrical[19] isomers. *cis*- and *trans*-$[Cr(ONO)_2(tn)_2]ClO_4$ exhibit the ν(N=O) bands at 1500 and 1470 cm^{-1}, respectively and no band assignable to the $\rho_w(NO_2)$ vibration, although the ν(N–O) bands which are expected to appear around 1100 cm^{-1} are masked by the absorption of the perchlorate anion. Thus the NO_2^- ligand is considered to have the Cr–O linkage in both isomers as is known for all other chromium(III)–nitrite complexes. The Cr–N linkage of the thiocyanate ligand in *cis*- and *trans*-$[Cr(NCS)_2(tn)_2]SCN$ is also suggested by IR

Table 1. Analytical data for the bis(trimethylenediamine)chromium(III) complexes

Complex	Found, %			Calcd, %		
	C	H	N	C	H	N
cis-$[Cr(NCS)_2(tn)_2]SCN\cdot H_2O$	27.80	5.80	24.79	27.53	5.64	24.99
$(+)_{589}$-*cis*-$[Cr(NCS)_2(tn)_2]SCN$	28.35	5.41	25.65	28.87	5.38	26.18
$(-)_{589}$-*cis*-$[Cr(NCS)_2(tn)_2]SCN$	28.55	5.29	25.92			
trans-$[Cr(NCS)_2(tn)_2]SCN$	28.89	5.55	25.53			
$(+)_{589}$-*cis*-$[Cr(NCS)_2(en)_2]SCN$	24.65	4.66	27.90	24.27	4.66	28.30
cis-$[Cr(H_2O)_2(tn)_2](NO_3)_3$	17.27	5.80	23.13	17.07	5.76	23.33
trans-$[Cr(H_2O)_2(tn)_2](NO_3)_3$	17.06	5.81	23.30			
cis-$[CrOH(H_2O)(tn)_2](NO_3)_2\cdot 0.5H_2O$	19.56	6.57	22.68	19.57	6.57	22.82
trans-$[CrOH(H_2O)(tn)_2](NO_3)_2$	20.01	6.42	23.07	20.06	6.45	23.39
cis-$[Cr(ONO)_2(tn)_2]ClO_4$	18.15	5.15	20.95	18.40	5.15	21.46
trans-$[Cr(ONO)_2(tn)_2]ClO_4$	18.51	5.30	20.79			
cis-$[Cr(N_3)_2(tn)_2]ClO_4$	18.81	5.32	36.13	18.78	5.25	36.50
$(+)_{589}$-*cis*-$[Cr(N_3)_2(tn)_2]ClO_4$	18.77	5.25	36.09			
trans-$[Cr(N_3)_2(tn)_2]ClO_4$	18.45	5.29	36.10			
$(-)_{589}$-*cis*-$[Cr(N_3)_2(tn)_2]ClO_4$	13.76	4.42	39.00	13.51	4.53	39.38

spectra, the ν(C≡N) and δ(NCS) bands appearing at around 2090 and 480 cm^{-1}, respectively in either isomer.

Baldwin's criterion[20] to distinguish between geometrical isomers was successful for many dianionobis(trimethylenediamine)cobalt(III) complexes,[9,21] trans isomers exhibiting one peak and cis isomers two in the CH$_2$-rocking (880—900 cm^{-1}) region. However all of the present chromium(III) complexes except *trans*-[Cr(ONO)$_2$(tn)$_2$]ClO$_4$ have single peak in the 880—895 cm^{-1} region irrespective of the geometrical structure, invalidating the Baldwin's criterion.

Hughes and McWhinnie examined the IR spectra of eleven bis(ethylenediamine)chromium(III) complexes including four cis-trans couples, and found the clearest distinction in the band pattern in the 550—395 cm^{-1} region.[22] Figures 1 and 2 show the IR spectra in the lower frequency region of four isomeric pairs of bis(trimethylenediamine)chromium(III) complexes. The complexity in the band pattern for each cis isomer compared with that for the corresponding trans isomer is apparent in the 550—330 cm^{-1} region. Thus discrimination between cis and trans isomers seems possible in these cases if the couple is presented, whereas it will be quite difficult to assign the geometrical structure on the IR data when only one isomer is obtained.[23]

Absorption and CD Spectra. Table 2 collects the absorption data for the present complexes. The molar absorbance of each cis isomer in the first d-d band is a little larger than that of the trans isomer except for the diazido complexes. Similar trend has frequently been reported for bis(ethylenediamine)chromium(III) complexes.[24] It is noteworthy in the present complexes that the energy difference between the first and second bands is larger for the trans isomer than for the cis isomer (Table 2).

In the case of dianionobis(trimethylenediamine)cobalt(III) complexes, the absorption maxima of the first band exist in appreciably lower energy region as compared with those of the corresponding ethylenediamine complexes, indicating the weak ligand field of trimethylenediamine relative to ethylenediamine.[9,21] In the case of chromium(III) complexes, the same trend is observed but the difference is quite small.

TABLE 2. ELECTRONIC ABSORPTION DATA FOR THE BIS(TRIMETHYLENEDIAMINE)CHROMIUM(III) COMPLEXES

Complex	Solvent	$\frac{\lambda_{max}}{nm}$ $\left(\frac{\varepsilon_{max}}{l\cdot mol^{-1}\cdot cm^{-1}}\right)$	$\frac{\Delta\nu_{12}{}^{a)}}{10^3\ cm^{-1}}$
cis-[Cr(NCS)$_2$(tn)$_2$]SCN·H$_2$O	CH$_3$OH	498 (109)	6.23
		380 (66.4)	
		318 (6560)	
		268 (4720)	
		233 (13500)	
trans-[Cr(NCS)$_2$(tn)$_2$]SCN	CH$_3$OH	510 (94.5)	6.85
		378 (69.7)	
		316 (10000)	
		263sh (4950)	
		237 (15400)	
cis-[Cr(H$_2$O)$_2$(tn)$_2$](NO$_3$)$_3$	1M HNO$_3$	490 (41.8)	6.91
		366 (37.0)	
trans-[Cr(H$_2$O)$_2$(tn)$_2$](NO$_3$)$_3$	1M HNO$_3$	520sh (19.6)	7.94
		452 (28.8)	
		368 (42.1)	
cis-[Cr(ONO)$_2$(tn)$_2$]ClO$_4$	H$_2$O	488 (49.7)	7.44
		358 (103)	
		245sh	
		235sh	
trans-[Cr(ONO)$_2$(tn)$_2$]ClO$_4$	H$_2$O	485 (43.2)	9.68
		366sh	
		330 (174)	
		266sh	
		250sh	
		237sh	
cis-[Cr(N$_3$)$_2$(tn)$_2$]ClO$_4$	H$_2$O	520 (136)	5.77
		400 (115)	
		270 (5670)	
		225 (12100)	
trans-[Cr(N$_3$)$_2$(tn)$_2$]ClO$_4$	H$_2$O	544 (157)	6.74
		398 (97.1)	
		278 (5290)	
		250sh	
		228 (10100)	

a) Difference in wave numbers between the first and second absorption maxima.

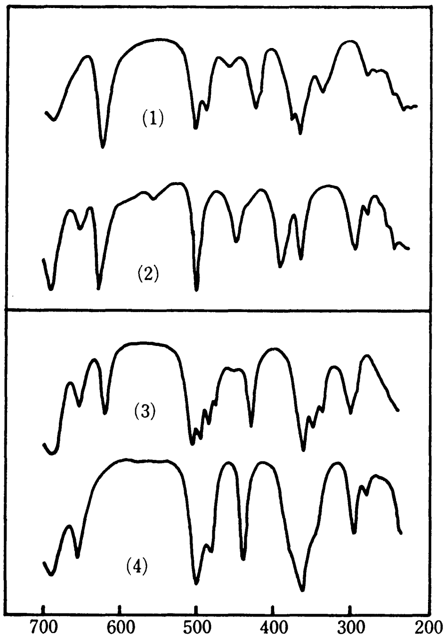

Fig. 1. Infrared spectra (700—200 cm^{-1}) in Nujol of *cis*-$[Cr(ONO)_2(tn)_2]ClO_4$ (1), *trans*-$[Cr(ONO)_2(tn)_2]ClO_4$ (2), *cis*-$[Cr(NCS)_2(tn)_2]SCN$ (3), and *trans*-$[Cr(NCS)_2(tn)_2]SCN$ (4).

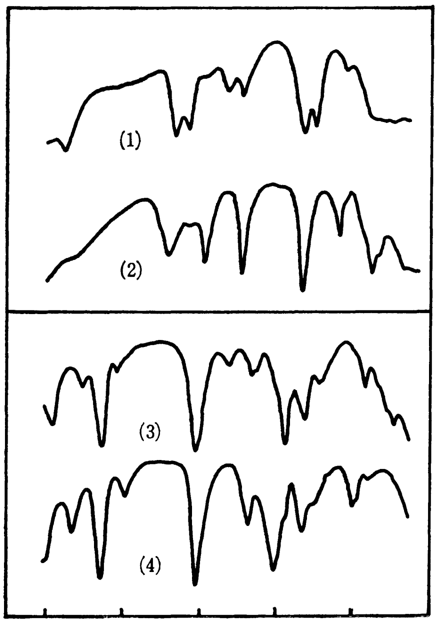

Fig. 2. Infrared spectra (700—200 cm^{-1}) in Nujol of *cis*-$[Cr(H_2O)_2(tn)_2](NO_3)_3$ (1), *trans*-$[Cr(H_2O)_2(tn)_2](NO_3)_3$ (2), *cis*-$[Cr(N_3)_2(tn)_2]ClO_4$ (3), and *trans*-$[Cr(N_3)_2(tn)_2]ClO_4$ (4).

Thus the largest value of difference in λ_{max} is 14 nm observed between *trans*-$[CrCl_2(tn)_2]Cl$ (590 nm) and *trans*-$[CrCl_2(en)_2]Cl$ (576 nm), and in the case of *cis*-diisothiocyanato and *cis*-diazido complexes depicted in Figs. 3 and 4, respectively, the difference is negligibly small (2 nm).

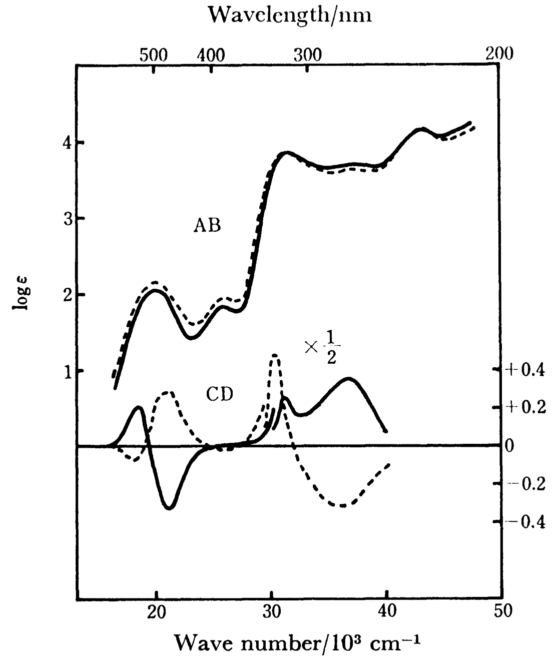

Fig. 3. Absorption and CD spectra of $(+)_{589}$-*cis*-$[Cr(NCS)_2(tn)_2]SCN$ (——) and $(+)_{589}$-*cis*-$[Cr(NCS)_2(en)_2]SCN$ (- - -) in methanol.

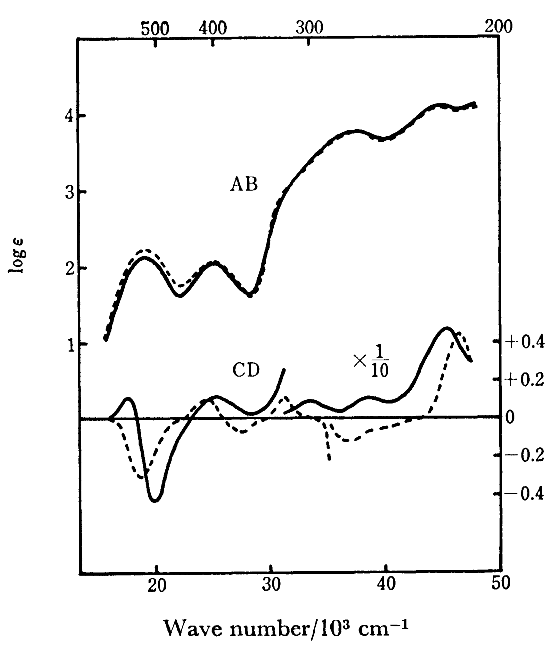

Fig. 4. Absorption and CD spectra of $(+)_{589}$-*cis*-$[Cr(N_3)_2(tn)_2]ClO_4$ (——) and $(-)_{589}$-*cis*-$[Cr(N_3)_2(en)_2]ClO_4$ (- - -) in water.

Figures 3 and 4 also compare the CD spectra of the diisothiocyanato- and diazido–bis(diamine) complexes. Although the intensity of the positive CD band of $(+)_{546}$-$[Cr(tn)_3](ClO_4)_3$ in the first d-d absorption band region ($\Delta\varepsilon = +0.34$ at 20.9×10^3 cm^{-1} in water) is remarkably smaller than that of $(+)_{546}$-$[Cr(en)_3](ClO_4)_3$ ($\Delta\varepsilon = +1.49$ at 21.9×10^3 cm^{-1} in water),[25] the intensities of CD bands in the same region of $(+)_{589}$-

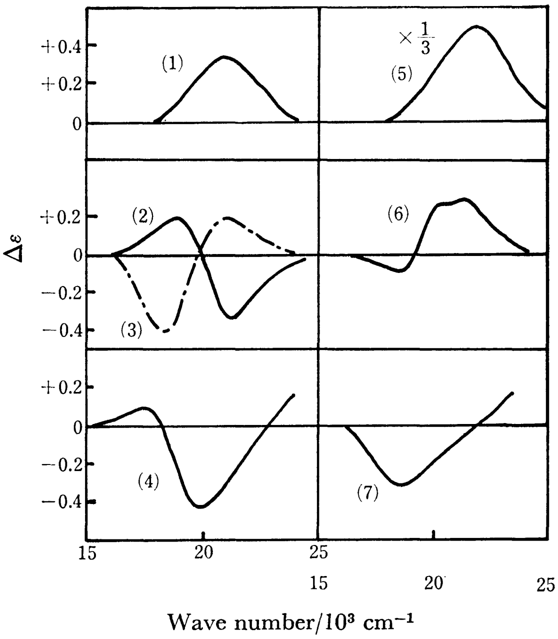

Fig. 5. CD bands in the first d-d absorption region of $(+)_{546}$-[Cr(tn)$_3$](ClO$_4$)$_3$ in water (1),[25] $(+)_{589}$-*cis*-[Cr(NCS)$_2$(tn)$_2$]SCN in methanol (2), Λ-$(-)_{589}$-*cis*-[Co(NCS)$_2$(tn)$_2$]SCN in water (3),[9] $(+)_{589}$-*cis*-[Cr(N$_3$)$_2$(tn)$_2$]ClO$_4$ in water (4), $(+)_{546}$-[Cr(en)$_3$](ClO$_4$)$_3$ in water (5),[25] $(+)_{589}$-*cis*-[Cr(NCS)$_2$(en)$_2$]SCN in methanol (6), and $(-)_{589}$-*cis*-[Cr(N$_3$)$_2$(en)$_2$]ClO$_4$ in water (7).

cis-[Cr(NCS)$_2$(tn)$_2$]SCN and $(+)_{589}$-*cis*-[Cr(N$_3$)$_2$(tn)$_2$]ClO$_4$ are rather larger than those of the corresponding ethylenediamine complexes. Another feature to be noted is that $(+)_{589}$-*cis*-[Cr(N$_3$)$_2$(tn)$_2$]ClO$_4$ exhibits two CD components in this region, whereas $(-)_{589}$-*cis*-[Cr(N$_3$)$_2$(en)$_2$]ClO$_4$ only one.

Figure 5 compares the CD spectra of the bis(diamine) complexes in the first d-d absorption region with those of the tris(diamine) complexes. The CD pattern of $(+)_{589}$-*cis*-[Cr(NCS)$_2$(tn)$_2$]SCN is just opposite to that of $(-)_{589}$-*cis*-[Co(NCS)$_2$(tn)$_2$]SCN[9] which was confirmed by X-ray analysis to have the Λ configuration.[26] Thus the absolute configuration of $(+)_{589}$-*cis*-[Cr(NCS)$_2$(tn)$_2$]SCN is readily assigned to Δ. On the same reasoning $(+)_{589}$-*cis*-[Cr(NCS)$_2$(en)$_2$]$^+$ was concluded to be Λ by House.[12] The dominant CD band of this ethylenediamine complex is positive in accord with the CD band of Λ-[Cr(en)$_3$](ClO$_4$)$_3$ in this region.[25] On the contrary $(-)_{589}$-*cis*-[Cr(N$_3$)$_2$(en)$_2$]ClO$_4$ exhibits a negative band, suggesting the Δ configuration. The spectral pattern of $(+)_{589}$-*cis*-[Cr(N$_3$)$_2$(tn)$_2$]ClO$_4$ closely resembles that of $(+)_{589}$-*cis*-[Cr(NCS)$_2$(tn)$_2$]SCN, both having the dominant negative component in the higher energy region. Thus the absolute configuration of $(+)_{589}$-*cis*-[Cr(N$_3$)$_2$(tn)$_2$]ClO$_4$ is assigned to Δ in accordance with the Δ configuration of $(-)_{589}$-*cis*-[Cr(N$_3$)$_2$(en)$_2$]ClO$_4$.

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