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# Trimethylenediamine Complexes. II. Some *cis-trans* Isomeric Pairs of Diacidobis(trimethylenediamine)cobalt(III) Complexes*[1]

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Isomeric pairs of *cis*- and *trans*-dinitro-, diisothiocyanato- and cyanosulfito-bis(trimethylenediamine)cobalt(III) complexes, and *cis*-nitronitritobis(trimethylenediamine)cobalt(III) nitrite were synthesized. Their electronic and infrared spectra were compared with each other to assign their structures. The *cis*-diisothiocyanatobis(trimethylenediamine)cobalt(III) complex was resolved into optically active isomers by means of potassium antimony(III) (+)-tartrate. The circular dichroism spectra of this dissymmetric complex were measured and discussed in relation to its absolute configuration which was recently determined by X-ray analysis.

Several diacidobis(trimethylenediamine)cobalt(III) complexes were derived from *trans*-dichlorobis(trimethylenediamine)cobalt(III) chloride by the ligand substitution reactions in methanol, and all of them were assumed to have the *trans* configuration on the basis of their infrared data.[1] It is curious that there are very few reports on trimethylenediamine complexes. No example of *cis-trans* isomeric pairs of the diacidobis(trimethylenediamine)cobalt(III) complex is known. We tried to prepare these compounds and report three such pairs obtained so far.

## Experimental

***cis*-Dinitrobis(trimethylenediamine) cobalt (III) Nitrite.** Five grams of *trans*-[$CoCl_2tn_2$]Cl was dissolved in a small quantity of hot water, to which 12 g of potassium nitrite was added. The solution was heated for about 3 hr and then kept standing overnight at room temperature. Crude precipitate was recrystallized from water, washed with water and then with acetone and dried in air. Orange-yellow crystals (3.5 g) were obtained.

Found: C, 20.60; H, 5.88; N, 27.11%. Calcd for $C_6H_{20}N_7O_6Co$=[$Co(NO_2)_2tn_2$]$NO_2$: C, 20.88; H, 5.84; N, 27.40%.

The same compound was also obtained by heating an aqueous solution of *trans*-[$Co(NO_2)_2tn_2$]$NO_2$ for a few hours.

When excess sodium nitrite was added to an aqueous solution of [$CoCO_3tn_2$]Cl and kept standing for 4 days at room temperature, or heated for 3 hr on a hot water bath, color of the solution turned from purple to reddish brown, and orange-yellow crystals appeared which were recrystallized from hot water. The infrared spectrum of this specimen was also identical with that of *cis*-[$Co(NO_2)_2tn_2$]$NO_2$ prepared by the above method.

***cis*-Nitronitritobis(trimethylenediamine)cobalt(III) Nitrite.** Five grams of *trans*-[$CoCl_2tn_2$]Cl was dissolved in a small quantity of hot water, to which 12 g of potassium nitrite was added. The solution was heated for about 1 hr and then cooled for a few hours. Deposited crystals were washed with cold water and then with methanol and dried. Orange yellow crystals (3.1 g) were obtained.

Found: C, 20.88; H, 6.10; N, 27.46%.

***cis*-Diisothiocyanatobis(trimethylenediamine)-cobalt(III) Thiocyanate.** To a hot aqueous solution (*ca.* 70 m*l*) of *trans*-[$CoCl_2tn_2$]Cl (5 g) was added gradually an aqueous solution (*ca.* 30 m*l*) of potassium thiocyanate (15 g). When the solution was heated for about 15 min, orange red crystals precipitated which were filtered off after cooling in ice for 2 hr, and recrystallized from hot water. Yield: 3.0 g.

Found: C, 28.41; H, 5.36; N, 25.53%. Calcd for $C_9H_{20}N_7S_3Co$=[$Co(NCS)_2tn_2$]SCN: C, 28.34; H, 5.29; N, 25.70%.

*trans*-Dinitro- and *trans*-diisothiocyanato-complexes were derived from *trans*-[$CoCl_2tn_2$]Cl by the ligand substitution reactions in methanol as reported[1].

***cis*-Cyanosulfitobis(trimethylenediamine)cobalt(III).** This compound was prepared by following the method which Ohkawa, Hidaka and Shimura[2] had employed in synthesizing *cis*-[$CoCN(SO_3)en_2$]. To a 10 % aqueous solution of $Na_3[Co(CN)_2(SO_3)_2(NH_3)_2]\cdot 6H_2O$ (10 g), 10 g of trimethylenediamine was added. The solution was heated on a hot water bath for 5—10 hr, and then concentrated by slow evaporation to separate yellow brown crystals (1.1 g).

Found: C, 26.93; H, 6.75; N, 22.03%. Calcd for $C_7H_{20}N_5SO_3Co$=[$CoCN(SO_3)tn_2$]: C, 26.84; H, 6.49; N, 22.36%.

**Sodium Disulfitobis(trimethylenediamine)-cobaltate(III) Trihydrate.** Baldwin's method[3] of preparing the corresponding ethylenediamine complex

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*[1] Partly presented at the 10th International Conference on the Coordination Chemistry, Nikko, Japan, September, 1967.

[1] H. Kawaguchi, N. Yano and S. Kawaguchi, This Bulletin, **42**, 136 (1969).

[2] K. Ohkawa, J. Hidaka and Y. Shimura, *ibid.*, **39**, 1715 (1966).

[3] M. E. Baldwin, *J. Chem. Soc.*, **1961**, 3123.

was followed. Five grams of sodium sulfite was dissolved in *ca.* 50 m*l* of hot water, to which 3 g of solid *trans*-[$CoCl_2tn_2$]Cl was added. Orange yellow precipitate resulted, which was filtered off and recrystallized from water by adding sodium sulfite solution and ethanol.

Found: C, 16.29; H, 6.09; N, 12.86%. Calcd for $C_6H_{26}N_4S_2O_9CoNa = Na[Co(SO_3)_2tn_2]\cdot 3H_2O$: C, 16.22; H, 5.90; N, 12.61%.

**Chlorosulfitobis(trimethylenediamine)cobalt(III) Monohydrate.** $Na[Co(SO_3)_2tn_2]\cdot 3H_2O$ was kneaded with concentrated hydrochloric acid. Sulfur dioxide gas was evolved and the color changed to pink. The solid mass was washed with methanol, dissolved in 6 N hydrochloric acid, and recrystallized by adding methanol to this solution.

Found: C, 21.34; H, 6.72; N, 16.34%. Calcd for $C_6H_{22}N_4SO_4ClCo = [CoCl(SO_3)tn_2]\cdot H_2O$: C, 21.15; H, 6.51; N, 16.44%.

***trans*** **- Cyanosulfitobis(trimethylenediamine) - cobalt(III) Monohydrate.** To a 10 % aqueous solution of $[CoCl(SO_3)tn_2]\cdot H_2O$ was added a concentrated solution of equimolar potassium cyanide. Yellow brown precipitate was produced but dissolved again upon prolonged stirring. To this solution five or six times the volume of ethanol was added and kept at 0°C. Yellow brown needles separated were recrystallized from water by adding ethanol. This method of preparation is analogous to that for the corresponding ethylenediamine complex.[4]

Found: C, 25.23; H, 6.79; N, 20.99%. Calcd for $C_7H_{22}N_5SO_4Co = [CoCN(SO_3)tn_2]\cdot H_2O$: C, 25.38; H, 6.69; N, 21.14%.

***cis*** **- Dicyanobis(trimethylenediamine)cobalt(III) Thiosulfate.** Yellow needles were obtained according to the method of Ohkawa *et al.*[5]

Found: C, 30.45; H, 6.49; N, 26.39%. Calcd for $C_{16}H_{40}N_{12}S_2O_3Co_2 = [Co(CN)_2tn_2]_2S_2O_3$: C, 30.47; H, 6.39; N, 26.66%.

***cis*****- Chloroaquobis (trimethylenediamine)cobalt(III) Chloride.** Two grams of carbonatobis(trimethylenediamine)cobalt(III) chloride monohydrate, which had been synthesized according to Werner's method,[6] was wetted with several drops of water and cooled with ice and salt. To this mass was added cold concentrated hydrochloric acid drop by drop until the evolution of carbon dioxide ceased. The purple solution was cooled with ice and salt and cold acetone was added to separate pink power. The product was filtered off, washed with cold acetone and dried over phosphorus pentaoxide *in vacuo*.

Found: C, 21.73; H, 6.82; N, 16.53; Cl, 31.60; $H_2O$ (by the Karl Fischer method), 5.23%. Calcd for $C_6H_{22}N_4OCl_3Co = [CoCl(H_2O)tn_2]Cl_2$: C, 21.30; H, 6.69; N, 16.56; Cl, 32.09; $H_2O$, 5.44%.

**The Optical Resolution of *cis*-[$Co(NCS)_2tn_2$]SCN.** The sample was dissolved in a minimum quantity of water, to which large excess of potassium iodide was added and cooled with ice to precipitate *cis*-[$Co(NCS)_2tn_2$]I. Two grams of this iodide was mixed with 0.74 g (equimolar) of silver acetate in the presence of a small amount of water. A small quantity of cold water was added and silver iodide was filtered off. To the filtrate was added 0.74 g (half molar) of potassium antimony(III)(+)-tartrate and the solution was kept standing overnight in an ice bath. Separated $(-)_D$-*cis*-[$Co(NCS)_2tn_2$][Sb(+)-tart] was dissolved again in a minimum volume of water. A large excess of potassium iodide was added and the solution was cooled in an ice bath to precipitate $(-)_D$-*cis*-[$Co(NCS)_2tn_2$]I. The optical-active compound was treated with silver acetate again. After silver iodide was filtered off, excess potassium thiocyanate was added to the filtrate to precipitate $(-)_D$-*cis*-[$Co(NCS)_2tn_2$]SCN.

**Spectral Measurements.** Electronic absorption spectra were measured by means of a Hitachi spectrophotometer model EPS-2. Infrared absorption spectra in the region from 4000 through 650 cm$^{-1}$ were measured with a Hitachi infrared spectrophotometer EPI-2, and those in 700—200 cm$^{-1}$ with a Hitachi grating infrared spectrophotometer EPI-L. The optical rotatory dispersion curve was determined by means of a Yanagimoto spectropolarimeter model ORD-185 and the circular dichroism curve with a Roussel-Jouan dichrograph.

## Results and Discussion

Hughes and McWhinnie[7] compared the infrared spectra of various *cis*- and *trans*-diacidobis(ethylenediamine)cobalt(III) complexes in the lower frequency region and reported that the Co–N (en) stretching peaks in the 600—500 cm$^{-1}$ region

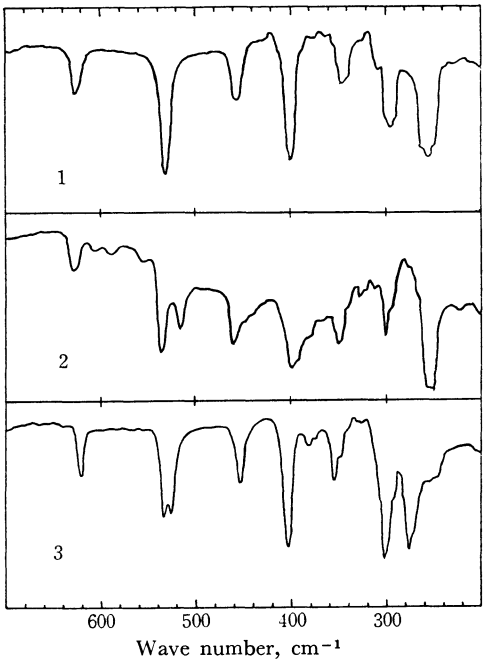

Fig. 1. Infrared spectra in the 700—200 cm$^{-1}$ region.
(1) *trans*-[$Co(NO_2)_2tn_2$]$NO_2$
(2) *cis*-[$CoNO_2(ONO)tn_2$]$NO_2$
(3) *cis*-[$Co(NO_2)_2tn_2$]$NO_2$

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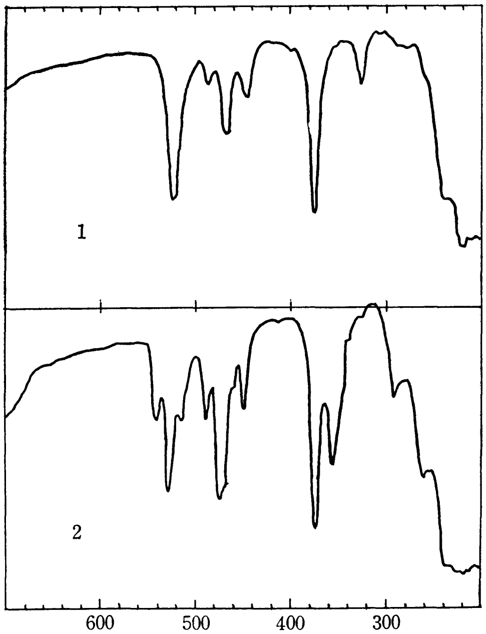
[4] S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, **1963**, 966.

[5] K. Ohkawa, J. Fujita and Y. Shimura, This Bulletin, **38**, 66 (1965).

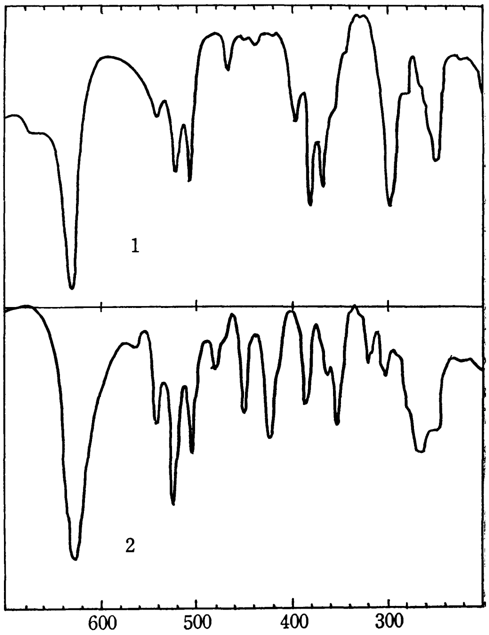
[6] A. Werner, *Ann.*, **386**, 264 (1912).

[7] M. N. Hughes and W. R. McWhinnie, *J. Inorg. Nucl. Chem.*, **28**, 1659 (1966).



Wave number, cm$^{-1}$

Fig. 2. Infrared spectra of $[Co(NCS)_2tn_2]SCN$ in the 700—200 cm$^{-1}$ region.
(1) the *trans* form
(2) the *cis* form



Wave number, cm$^{-1}$

Fig. 3. Infrared spectra of $[CoCN(SO_3)tn_2]$ in the 700—200 cm$^{-1}$ region.
(1) the *trans* form
(2) the *cis* form

were most helpful in diagnosing the geometrical configuration. In Figs. 1, 2 and 3 are presented the infrared absorption bands in the lower frequency region of the three isomeric pairs of compounds we prepared. The infrared absorption bands of these complexes are rather simple in comparison with those of diacidobis(ethylenediamine) complexes reported by Hughes and McWhinnie.[7] In the present case, too, spectra of *cis* and *trans* isomers are not identical, but the former are more complicated than the latter.

Although the reaction between *trans*-$[CoCl_2tn_2]$-Cl and excess potassium nitrite in hot methanol gave *trans*-$[Co(NO_2)_2tn_2]NO_2$, the same reaction in hot water resulted in a *cis* isomer. The *trans* form shows a single peak of Co–N(tn) stretching at 531 cm$^{-1}$, but the *cis* isomer two peaks at 531 and 524 cm$^{-1}$. In the synthetic study of this system an interesting phenomenon was observed. When a concentrated aqueous solution of excess potassium nitrite was added under stirring to an aqueous solution of *trans*-$[CoCl_2tn_2]Cl$ at room temperature or even at 0°C, yellow precipitate separated at first which was identified as potassium hexanitrocobaltate(III). However, prolonged agitation of the reaction mixture resulted in a gradual decrease of the yellow compound and increase of an orange brown precipitate which was *trans*-$[Co(NO_2)_2tn_2]NO_2$. It seems strange that two molecules of trimethylenediamine easily displaced by nitrite anions actually make a counterattack and replace the nitrite groups. Such reactions have never been recognized in bis(ethylenediamine)cobalt(III) complexes.

It should also be noted that in reactions between hexanitrocobaltate(III) and trimethylenediamine, *trans*-$[Co(NO_2)_2tn_2]NO_2$ precipitates at room temperature, but the corresponding *cis* complex is formed at higher temperatures. If crystals of the *trans* form is redissolved in water and heated, the *cis* form is obtained. However, the reverse isomerization from *cis* to *trans* has not yet been realized.

When the heating time was relatively short, *e.g.* 1 hr, the reaction between *trans*-$[CoCl_2tn_2]Cl$ and excess potassium nitrite in water gave orange crystals. Analytical data of this compound agree with those for the dinitro complex, but its infrared spectra differ from those of *cis*- and *trans*-$[Co(NO_2)_2$-$tn_2]NO_2$. As shown in Fig. 1 two peaks due to the Co-N(tn) stretching vibration are observed at 529 and 516 cm$^{-1}$ suggesting the *cis* configuration of this compound. Absorption due to the wagging vibration of the nitro group[8] appears as a single peak both for *cis* and *trans* dinitro complexes. However, three peaks are observed for the new compound. A strong peak exists at 1170 cm$^{-1}$ which is not shown by dinitro complexes and disappears on heating. The results strongly suggest that this compound is a linkage isomer, *cis*-$[CoNO_2(ONO)$-$tn_2]NO_2$. As reported previously, *trans*-$[CoCl$-$(ONO)tn_2]Cl$ is labile and isomerizes quickly in methanol and so the absorption spectrum could not be observed at room temperature. The *cis*-nitronitrito compound, on the other hand, is rather inert and the isomerization to the dinitro isomer is slow even in a hot aqueous solution.

The absorption spectra of *cis*- and *trans*-$[Co(NO_2)_2tn_2]NO_2$ and *cis*-$[CoNO_2(ONO)tn_2]NO_2$ in methanol are presented in Fig. 4. It seems unlikely that the *cis*- and *trans*- dinitro complexes show practically identical spectra. The *cis*-*trans* isomerization equilibrium cannot possibly be attained so quickly in methanol at room temperature. The transmission spectra of solid specimen of both compounds, measured by the Nujol mull method, are also identical. The first band of the nitro-nitrito complex lies at the slightly longer wavelength side than that of the dinitro isomer (Table 1). The same trend is observed for the corresponding ethylenediamine complexes.[9]

The absorption spectra of *cis*- and *trans*-$[Co(NCS)_2tn_2]SCN$ are shown in Fig. 5. The first band of the *trans* isomer lies on the longer wavelength side than that of the *cis* isomer. This is contrary to the observation on the corresponding ethylenediamine complexes.[10] When *cis*-$[Co(NCS)_2tn_2]SCN$ was dissolved in methanol, heated for a few hours, and then concentrated by evaporation, crystals of the *trans* isomer were obtained. Reverse isomerization from *trans* to *cis* was not possible.

The infrared spectra of *cis*- and *trans*-[CoCN-

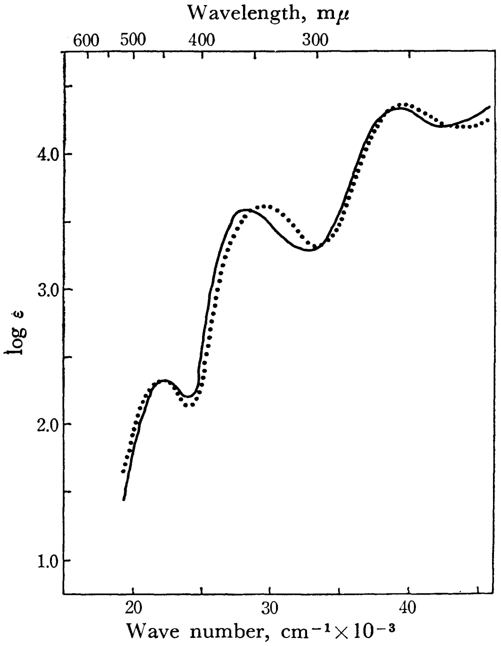


Fig. 4. Absorption spectra in methanol.
—— *trans*- and *cis*-$[Co(NO_2)_2tn_2]NO_2$
···· *cis*-$[CoNO_2(ONO)tn_2]NO_2$

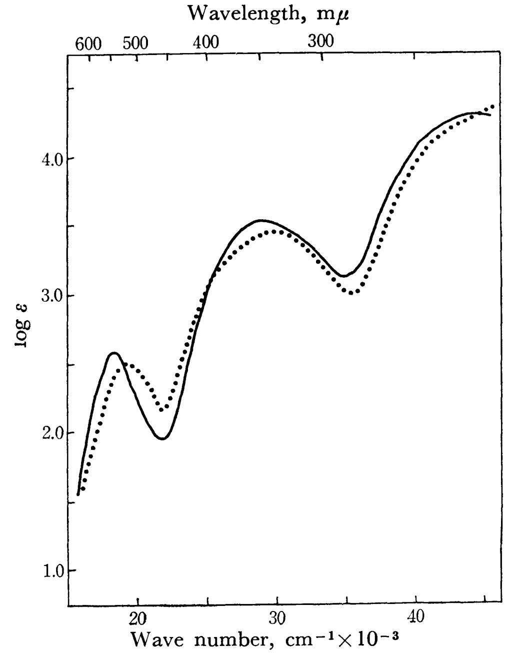


Fig. 5. Absorption spectra of $[Co(NCS)_2tn_2]$ SCN in methanol.
—— the *trans* form
···· the *cis* form

TABLE 1. ABSORPTION MAXIMA OF SOME BIS(TRIMETHYLENEDIAMINE)- AND BIS(ETHYLENEDIAMINE)COBALT(III) COMPLEXES

| Complex | Medium | $\lambda_{max}$, mμ(ε) | | |
|---|---|---|---|---|
| *cis*-$[CoNO_2(ONO)tn_2]NO_2$ | Methanol | 455(214) | 340(4900) | 253(22000) |
| *cis*-$[Co(NO_2)_2tn_2]NO_2$ | Methanol | 450(220) | 358(3890) | 256(21200) |
| *cis*-$[Co(NO_2)_2en_2]NO_3$[10] | MeOH-$H_2O$ | 438(220) | 325(5050) | 240(16600) |
| *cis*-$[Co(NCS)_2tn_2]SCN$ | Methanol | 522(319) | 340(2750) | |
| *cis*-$[Co(NCS)_2en_2]SCN$[10] | MeOH-$H_2O$ | 520(350) | 335(3400) | |
| *cis*-$[CoCN(SO_3)tn_2]$ | Water | 433(176) | 281(17000) | |
| *cis*-$[CoCN(SO_3)en_2]$[2] | 4% $NH_3$ *aq* | 417(162) | | |
| *trans*-$[CoCN(SO_3)tn_2]$ | Water | 433(148) | 280(17500) | 222(13400) |
| *trans*-$[CoCN(SO_3)en_2]$[2] | Water | 416(135) | | |

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8) I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **23A**, 2099 (1967).

9) R. G. Pearson, P. M. Henry, J. G. Bergmann and F. Basolo, *J. Amer. Chem. Soc.*, **76**, 5920 (1954).

10) F. Basolo, *ibid.*, **72**, 4393 (1950).

$(SO_3)tn_2]$ in the region of 600—500 cm$^{-1}$ are complicated and less diagnostic than those for dinitro and diisothiocyanato complexes (Fig. 3). The *cis* isomer has four peaks in this region, while the *trans* isomer three. The electronic absorption spectra of these compounds also resemble each other as shown in Fig. 6.

The absorption maxima of the new compounds reported here are summarized in Table 1 together with those of the corresponding ethylenediamine complexes. As in a previous paper,[1] the first band of each trimethylenediamine complex lies at the longer wavelength side than that of the corresponding ethylenediamine complex, indicating that the ligand field of trimethylenediamine is weaker than that of ethylenediamine.

Efforts to prepare *cis*-dichlorobis(trimethylenediamine)cobalt(III) complex have not been successful so far. Treatment of $[CoCO_3tn_2]Cl$ with concentrated hydrochloric acid at low temperatures resulted in a pink-colored compound $[CoCl(H_2O)tn_2]Cl_2$, which is unstable and changes gradually to the green dichloro complex. The infrared absorption curve of this chloroaquo complex in the potassium bromide region is complicated as shown in Fig. 7 suggesting a possible *cis* configuration. In this connection the spectrum of *cis*-$[Co(CN)_2tn_2]_2S_2O_3$ is also included in Fig. 7. Unfortunately the corresponding *trans* isomer has not been obtained so far, and the comparison of IR curves of this isomeric pair is not possible, but the splitting of the Co–N(tn) stretching band may be reconciled with the *cis* assignment by Ohkawa, *et al.*[5]

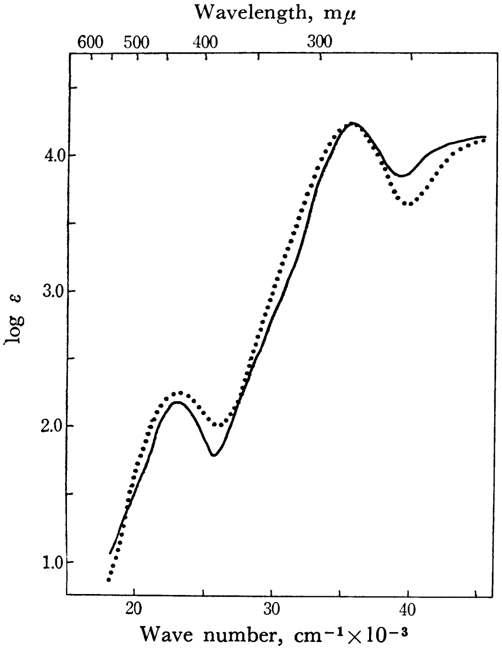

Fig. 6. Absorption spectra of $[CoCN(SO_3)tn_2]$ in water.

—— the *trans* form

···· the *cis* form

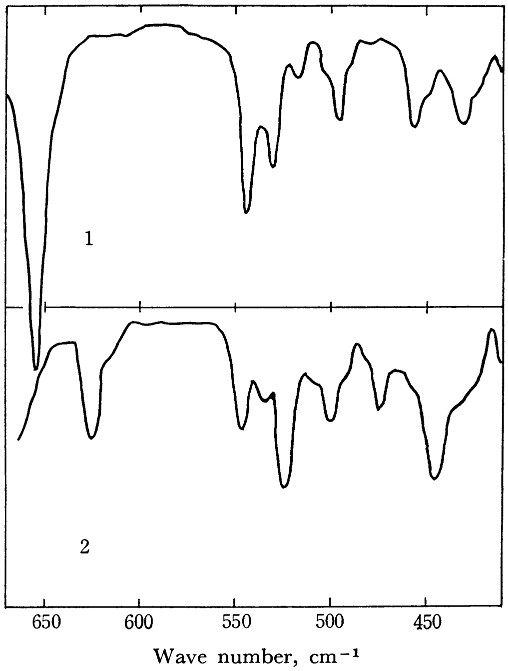

Fig. 7. Infrared spectra in the potassium bromide region.

(1) *cis*-$[Co(CN)_2tn_2]_2S_2O_3$

(2) *cis*-$[CoCl(H_2O)tn_2]Cl_2$

Hughes and McWinnie[7] compared several methods of diagnosing the geometrical configurations of diacidobis(ethylenediamine)cobalt(III) complexes, and showed that Baldwin's method[11] utilizing the $CH_2$ rocking peaks was the best among them. In Table 2 are summarized the $CH_2$ rocking peaks shown by bis(trimethylenediamine)-cobalt(III) complexes discussed in this paper. Baldwin's criterion is successful in these examples except for one case, *cis* compounds showing two

TABLE 2. INFRARED ABSORPTION BANDS DUE TO THE $CH_2$ ROCKING VIBRATION OF SEVERAL *cis*- AND *trans*-DIACIDO-BIS(TRIMETHYLENEDIAMINE) COBALT(III) COMPLEXES

| Compound | cm$^{-1}$ | | |
|---|---|---|---|
| *cis*-$[CoNO_2(ONO)tn_2]NO_2$ | 895 | | 887 |
| *cis*-$[Co(NO_2)_2tn_2]NO_2$ | 902 | | 894 |
| *trans*-$[Co(NO_2)tn_2]NO_2$ | | 899 | |
| *cis*-$[Co(NCS)_2tn_2]SCN$ | 895 | | 890 |
| *trans*-$[Co(NCS)_2tn_2]SCN$ | | 890 | |
| *cis*-$[CoCN(SO_3)tn_2]$ | 905 | | 890 |
| *trans*-$[CoCN(SO_3)tn_2]$ | | 900 | |
| $[CoCO_3tn_2]Cl\cdot H_2O$ | 895 | | 888 |
| *cis*-$[CoCl(H_2O)tn_2]Cl_2$ | | 888 | |
| *cis*-$[Co(CN)_2tn_2]_2S_2O_3$ | 893 | | 887 |

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[11] M. E. Baldwin, *J. Chem. Soc.*, **1960**, 4369.

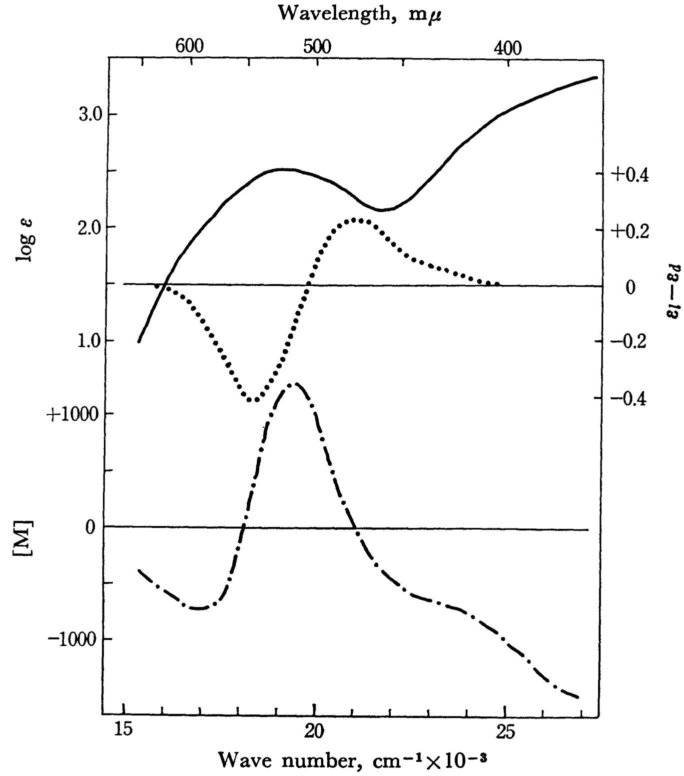

Fig. 8. Absorption(——), circular dichroism(····), and optical rotatory dispersion(·—·) curves of $(-)_D$-*cis*-$[Co(NCS)_2tn_2]SCN$ in water.

peaks while the *trans* isomers only one. The compound $[CoCl(H_2O)tn_2]Cl_2$, which was tentatively concluded to have the *cis* configuration, shows a single peak at 888 $cm^{-1}$ violating Baldwin's empirical rule.

To establish the *cis* configuration unequivocally we tried to resolve the *cis* compounds into their optical isomers, but have succeeded only in the case of *cis*-$[Co(NCS)_2tn_2]SCN$. In Fig. 8 are shown the rotatory dispersion and circular dichroism curves of the optically active isomer. The molar rotations were calculated as follows:

$$[M]^{23}_{546} = +275°;\ [M]^{23}_{589} = -725°$$

The first example of the optically active cobalt(III) trimethylenediamine complex is $(-)_D$-$Cotn_3^{3+}$ prepared by Woldby,[12] which was shown by Saito and his coworkers[13] to have the same absolute configuration as the $(+)_D$-$Coen_3^{3+}$ ion,[14] namely $\Delta$[15] or $P(C_2)$.[16] The crystal structure of the diastereoisomer $(-)_D$-$[Co(NCS)_2tn_2][Sb(+)$-tart$]\cdot 2H_2O$ has recently been studied and the absolute configuration of this dissymmetric complex cation was revealed to be $\Delta$ or $P(C_2)$, too.[17]

In recent years the circular dichroism spectra of a number of dissymmetric trigonal complexes have been measured and discussed in relation to their absolute configurations.[16] It was suggested[16,18] that trigonal $d^3$ and $d^6$ complexes have the same absolute configuration as $(+)_D$-$Coen_3^{3+}$ if the spin-allowed transition of lowest energy has an $E_a$ component with a positive rotatory power. Beddoe and Mason[19] showed that the $E_a$ component in $(-)_D$-$Cotn_3^{3+}$ has a positive rotational strength at longer wavelength, indicating that the spectroscopic criterion for the absolute configuration of trigonal metal complexes containing five-membered chelate rings may be successfully applicable to the trisdiamine complexes containing six-membered chelate rings. Consistent CD band assignments were also given by Gollogly and Hawkins to the enantiomeric $(+)_D$-$Cotn_3^{3+}$ ion.[20]

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[12] F. Woldby, *Record of Chemical Progress*, **24**, 197 (1963).

[13] Y. Saito, T. Nomura and F. Marumo, This Bulletin, **41**, 530 (1968).

[14] Y. Saito, K. Nakatsu, M. Shiro and H. Kuroya, *Acta Crystallogr.*, **8**, 729 (1955); This Bulletin, **30**, 158 (1957).

[15] *IUPAC Information Bulletin*, No. 33, 68 (1968).

[16] A. J. McCaffery, S. F. Mason and R. E. Ballard, *J. Chem. Soc.*, **1965**, 2883.

[17] K. Matsumoto, M. Yonezawa, H. Kuroya, H. Kawaguchi and S. Kawaguchi, This Bulletin, **43**, 1269 (1970).

[18] R. E. Ballard, A. J. McCaffery and S. F. Mason, *Proc. Chem. Soc.*, **1962**, 331.

[19] P. G. Beddoe and S. F. Mason, *Inorg. Nucl. Chem. Lett.*, **4**, 433 (1968).

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The relationship of absolute configuration to the optical activity of dissymmetric trigonal complexes have been extended to the *cis*-series of the bisethylenediamine complexes of cobalt(III). It was concluded that for the *cis*-complexes with the $P(C_2)$ configuration the major of the two CD bands mainly due to the $E_a$ component of the parent trigonal complex has a positive sign and is displaced less than the minor band from the reference frequency of the $\mathrm{Coen_3}^{3+}$ absorption.[21] The absolute configuration of $(+)_D$-$\mathrm{Co(CN)_2en_2}^+$ was determined by Matsumoto *et al.*[22] to be $\Lambda$ or $P$-$(C_2)$ in accordance with this assignment by McCaffery *et al.*[23]

As shown in Fig. 8 $(-)_D$-$\mathrm{Co(NCS)_2tn_2}^+$ gives two CD bands in the region of the long wavelength absorption band. The absolute rotational strengths of the bisdiamine complexes are usually smaller than those of the parent trisdiamine complexes owing to the reduced chelation,[24] but in the present case the CD bands of $(-)_D$-$\mathrm{Co(NCS)_2tn_2}^+$ are more than twice as intense as those of $(-)_D$-$\mathrm{Cotn_3}^{3+}$ (Fig. 9). If the above spectroscopic criterion concerning the absolute configurations of the bisethylenediaminecobalt(III) complexes can be extended to the bistrimethylenediamine complexes, the negative and the positive CD bands in Fig. 9 must be assigned to the $A_2$ and the $E_a$ transitions in $(-)_D$-$\mathrm{Cotn_3}^{3+}$, respectively. The positive high-energy component ($E_a$ parentage) is displaced only by 850 cm$^{-1}$ from the reference frequency of the $\mathrm{Cotn_3}^{3+}$ absorption, but the negative low-energy component ($A_2$ parentage) is much farther displaced (1850 cm$^{-1}$). Thus the frequency displacement criterion holds in this case, but the relative band-area criterion fails since the negative component is larger than the positive one.

Another method of identifying the CD bands due to $E_a$ and $A_2$ transition is based upon the observation that, in the presence of polarizable oxyanions such as phosphate, the areas of $E_a$ and $A_2$ bands in the trigonal complexes are diminished and enhanced, respectively.[25,26] Of the various oxyanions investigated, selenite was found to be particularly convenient, producing large changes in the band area.[27] This ion-pairing effect was successfully applied in the case of $\mathrm{Cotn_3}^{3+}$ ion,[19,20] but now gives inconsistent results to $(-)_D$-$\mathrm{Co(NCS)_2tn_2}^+$. As shown in Fig. 9 the effect of selenite addition upon the CD band areas is small but obvious. The negative low-energy component is diminished and the positive high-energy component enhanced indicating that they are of $E_a$ and $A_2$ trigonal parentage, respectively. Thus the CD bands assignment based on the outer-sphere coordination effect contradicts with the above assignment based on the empirical relationship between spectroscopic and configurational assignments. It is not certain at present which of them fails in the case of the bistrimethylenediamine complex, but the ion-pairing method might be less reliable. Further investigations of other dissymmetric trimethylenediamine complexes are desired.

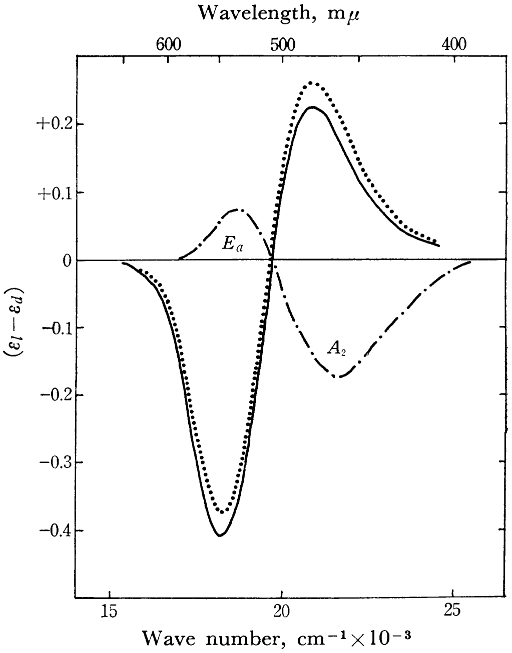

Fig. 9. Circular dichroism curves of $(-)_D$-*cis*-$[\mathrm{Co(NCS)_2tn_2}]\mathrm{ClO_4}$ in water(——) and in 0.05 M aqueous sodium selenite(····), and of $(-)_D$-$[\mathrm{Cotn_3}](\mathrm{ClO_4})_3$ in water(—·—).

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