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Stereochemical Studies of the Diammine(triethylenetetramine)cobalt(III) Complex

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All five possible geometrical and conformational isomers of the title complex have been isolated. Four of the five isomers, cis-α, cis-β-*RR,SS*, cis-β-*RS,SR*, and trans-*RR,SS*, can be resolved into optically active forms by SP-Sephadex column chromatography. They were identified by electronic absorption spectra, CD spectra, and ^{13}C NMR spectra and also by the synthesis of a stereospecifically formed trans isomer of a complex with a trien derivative, (2*S*,9*S*)-2,9-dimethyl-1,4,7,10-tetraazadecane.

Introduction

The stereochemistry of triethylenetetramine complexes has been extensively studied for the past two decades. In 1967, Sargeson and Searle[1] pointed out the possible existence of five geometrical and conformational isomers for complexes of the $[CoXX(trien)]^{n+}$ type (X, unidentate ligand). Although they investigated the stereochemistry of this type of complex[1] and examined the hydrolysis reaction of dichloro complexes in detail,[2,3] they could not get any evidence for the existence of the trans-meso isomer. Buckingham et al.[3] reported the possible existence of *cis-β-RS,SR*-$[Co(H_2O)_2(trien)]^{3+}$ in a solution of the hydrolysis product of *trans*-$[CoCl_2(trien)]^+$. The isomer was reported to be unstable and to isomerize to the cis-β-*RR,SS* isomer.[3] This has long been known as the only example of a cis-β-*RS,SR* isomer for complexes of the $[CoXX(trien)]^{n+}$ type, although it was not isolated as a solid complex salt. Since then, there have been no reports concerning the isolation and resolution of the complete set of the geometrical and conformational isomers except that of the diammine complex.[4] This report deals with the synthesis, isolation, optical resolution, and characterization of a set of isomers of $[Co(NH_3)_2(trien)]^{3+}$.

Experimental Section

The electronic spectra were obtained with a Shimadzu MPS-50L spectrophotometer. The CD spectra were measured with a JASCO J-40C spectropolarimeter.

Reagents. Commercially available triethylenetetramine was found to contain about 12% of triaminotriethylamine (tren), which was detected and estimated by ^{13}C NMR spectra. It was purified as follows. One hundred and ninety milliliters of 35% hydrochloric acid (2.23 mol) was stirred into a solution of trien (146 g; 1.0 mol in 1.0 L of ethanol) in small portions with cooling, and then the slurry was allowed to stand overnight in a refrigerator. The separated crystals of tren·3HCl were filtered with suction. In many runs, an average of 13.9 g (54 mmol) of the hydrochloride was obtained. To the filtrate was added another 160 mL of 35% hydrochloric acid. Precipitated trien·4HCl was filtered with suction and washed with five 500-mL portions of 75% ethanol and then ethanol and ether. Since this tetrahydrochloride was found to be practically pure, it was used as a ligand source without further purification.

A methyl derivative of trien, (2*S*,9*S*)-2,9-dimethyl-1,4,7,10-tetraazadecane (abbreviated as 2,9-dimetrien), was synthesized by a method described in the literature.[5]

Preparation of *cis*-α-Dinitro(triethylenetetramine)cobalt(III) Chloride and *cis*-α- and *cis*-β-Dichloro(triethylenetetramine)cobalt(III) Chloride. The procedures of Sargeson and Searle[1] were employed with a slight modification that, for the preparation of the dinitro complex, trien·4HCl and NaOH were used instead of trien and HCl. The yield of the dinitro complex was 81%, which was better than that reported.

Preparation of *trans*-Bis(isothiocyanato)(triethylenetetramine)cobalt(III) Complex. The procedures in the preceding paper[6] were employed without any modification.

Preparation and Optical Resolution of *cis*-α- and *cis*-β-Diammine(triethylenetetramine)cobalt(III) Perchlorate. To a mixture of 3.30 g (10 mmol) of *cis*-α-$[CoCl_2(trien)]Cl\cdot H_2O$, 3.6 g (67 mmol) of NH_4Cl, and 0.2 g of activated charcoal was added 20 mL of 1.0 M aqueous ammonia, and the resulting mixture was stirred overnight at room temperature. After the charcoal was filtered off, the filtrate and washings were combined, acidified with 5 mL of 1 M HCl, and diluted to 3 L. The diammine complex was adsorbed on a column (3.0 cm o.d. and 5 cm long) of SP-Sephadex C-25. The column was washed with water and then with 1 L of 0.03 M HCl. The complex was eluted with 0.5 M HCl, and the eluate was evaporated to dryness on a vacuum evaporator. A small amount of water was added to the residue, and evaporation was repeated. The residue was dissolved in 20 mL of water, and one-fifth of the solution was placed on a column (3.0 cm o.d. and 140 cm long) of SP-Sephadex C-25 and eluted with a 0.15 M solution of sodium sulfate. Two yellow bands were observed: the first was found to be *cis*-α-$[Co(NH_3)_2(trien)]^{3+}$, and the second to be *cis*-β-$[Co(NH_3)_2(trien)]^{3+}$.

The second fraction was chromatographed again with 0.15 M $Na_2[Sb_2((+)\text{-tart})_2]$ to give three yellow bands: the first was Λ-*cis*-β-*SS*-$[Co(NH_3)_2(trien)]^{3+}$, the second was Λ-*cis*-β-*SR*-$[Co(NH_3)_2(trien)]^{3+}$, and the third was a mixture of Δ-*cis*-β-*RR*- and Δ-*cis*-β-*RS*-$[Co(NH_3)_2(trien)]^{3+}$. The cis-α isomer was also resolved by using an SP-Sephadex column and 0.15 M $Na_2[Sb_2((+)\text{-tart})_2]$ as an eluent.

The cis-β isomers were prepared preferentially by the following method. Into 20 mL of 28% NH_3 were added 3.0 g of ammonium chloride and 3.3 g of *cis*-α-$[CoCl_2(trien)]Cl\cdot H_2O$, and the mixture was stirred until the solid complex disappeared. Thereafter the reaction mixture was allowed to stand overnight at room temperature. The resulting orange solution was deammoniated with a rotatory vacuum evaporator, and then it was acidified with 10 mL of 1 M HCl. The solution, which contained the cis-β isomers with a trace amount of the cis-α isomer, was diluted to 3 L and treated in the same way as above.

Preparation of *trans*-Diammine(triethylenetetramine)cobalt(III) Chloride or Perchlorate. The trans isomers were prepared by the reaction of the corresponding isothiocyanato complex with hydrogen peroxide.[7] To a solution of 210 mg (5 mmol) of *trans*-$[Co(NCS)_2(trien)]ClO_4$ in 40 mL of 0.1 M HCl was added 2.5 mL of 30% H_2O_2, and the mixture was allowed to stand for 4 days at 40 °C. The resulting yellow solution was diluted with 100 mL of water and treated in a manner similar to the solution used in the preparation of the *cis*-diammine isomers. The *rac* and the meso isomers were separated by SP-Sephadex column chromatography using acidic Na_2SO_4 as an eluent, and the *rac* isomer was resolved completely by SP-Sephadex chromatography using 0.15 M $Na_2[Sb_2((+)\text{-tart})_2]$ as an eluent.

Preparation of *trans*-Diammine((2*S*,9*S*)-2,9-dimethyl-1,4,7,10-tetraazadecane)cobalt(III) Complex. *trans*-$[Co(NCS)_2(2,9\text{-dimetrien})]ClO_4$ was prepared and isolated by a method analogous to the preparation of the corresponding trien complex. It was treated with hydrogen peroxide to give only one isomer of the *trans*-diammine complex.

Strain-Energy-Minimization Calculation. The strain energy of each isomer was calculated by using a modified Newton–Raphson method as developed by Boyd.[8] In the present study, the bond length force constants and nonbonded potential function constants have been retained from the original[9] or previous work,[4,10] and bond angle and torsional force constants were adopted from those published by DeHayes and Busch.[11] The nonbonded interactions between the atoms were treated up to distances of 1.4 times the sum of each van der Waals radius. The modi-

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Table I. Analytical and Electronic Spectral Data for $[Co(NH_3)_2(trien)](ClO_4)_3 \cdot nH_2O$

isomer	n		anal. % C	anal. % H	anal. % N	$\nu_{max}{}^b/10^3$ cm^{-1} I	$\nu_{max}{}^b/10^3$ cm^{-1} II
cis-α	0	found	13.3	4.2	15.8	21.1 (94)	29.4 (79)
		calcd	13.4	4.5	15.6		
Λ-cis-β-SS	0.5	found	13.0	4.4	15.3	21.2 (118)	29.3 (89)
		calcd	13.2	4.6	15.4		
Λ-cis-β-SR	1	found	13.3	4.0	15.7	21.1 (120)	29.3 (96)
		calcd	13.4	4.5	15.6		
(+)-trans-RR	1	found	13.0	4.5	15.0	21.4 (156)	29.2 (102)
		calcd	13.0	4.7	15.1		
trans-RS^a	1	found	19.8	7.0	23.1	21.6 (140)	29.2 (90)
		calcd	19.8	7.2	23.1		

^{a}Chloride instead of perchlorate. ^{b}Figures in parentheses are molar extinction coefficients.

fications were successfully applied to the $[Co(dien)_2]^{3+}$ system (dien: diethylenetriamine), in which a much higher stability of the *mer* isomer could not be explained in the previous calculations.[10,12]

Results and Discussion

Synthesis of the Isomers. The diammine(triethylenetetramine)cobalt(III) complex was first prepared by Kyuno and Bailar.[13] They obtained the cis-α isomer by a reaction of *cis*-α-$[CoCl_2(trien)]Cl$ with gaseous ammonia at 100 °C for 10 days and the cis-β isomer (possibly a mixture of two cis-β isomers) by a reaction of the *cis*-α-dichloro complex with liquid NH_3. These isomers have been found to be formed in an aqueous ammonia solution. When the reaction of the *cis*-α-dichloro complex with aqueous ammonia was carried out for 1 week in the presence of activated charcoal, the formation ratios of the cis-β-*RR,SS* and cis-β-*RS,SR* isomers were 1.32 and 0.79, respectively, based on the yield of the cis-α isomer. No sign of the formation of the trans isomers was found on the chromatograms of these samples. The trans isomers were derived by the reaction of *trans*-$[Co(NCS)_2(trien)]^+$ with hydrogen peroxide.

The ammine complex thus formed easily liberated ammonia in a neutral or a basic media to give aqua (or hydroxo) species. The ammonium chloride used in the synthesis served to prevent the decomposition of the diammine complex and to increase its yield.

Stereochemistry. Table I lists some properties of the isomers isolated in this study. Two cis-β isomers have been identified by the difference CD spectrum (DCD), which is shown in Figure 1. The DCD spectrum has two bands with opposite signs in the region of the first absorption band. It was reported that the rotational strengths due to several kinds of optical activities are additive for cobalt(III) complexes.[14] Although the additivity rule may be a crude approximation, it holds for several types of complexes.[15] The present cis-β isomers have three kinds of chiralities responsible for their CD spectra, i.e. the configurational chirality about the metal ion, the chiralities of two secondary nitrogen centers, and the conformational chiralities due to the chelate rings. Thus, the kinds of chiralities that two Λ-cis-β isomers possess are the configurational chirality of Λ, the nitrogen chiralities of S,S and the conformational chiralities of $\lambda\lambda\delta$ for the Λ-cis-β-SS isomer, and S,R and $\lambda\delta\lambda$ for the Λ-cis-β-SR isomer.[16] If the contribution of each chirality to the CD spectra can be assumed to be identical for the same type of chirality regardless of the position of nitrogens or chelate rings, the DCD spectrum (Λ-SS − Λ-SR) should have twice the contribution from the nitrogen of S configuration. Then, the DCD spectrum can be used as a useful tool to identify two cis-β isomers, if the absolute configurations of the isomers are known and the authentic DCD spectrum is given. Present cis-β isomers exhibit the CD spectra typical of Λ configuration, and they can be identified by comparing their DCD spectra with those of β_2-$[Co(glyO)(trien)]^{2+}$ isomers[17] and with those of β-$[Co(en)(penp)]^{3+}$ isomers (penp = 1,6-bis(2-pyridyl)-2,5-diazahexane).[18] It is interesting to note that the DCD spectrum seems to be independent of the difference in the chromophore of the complex.

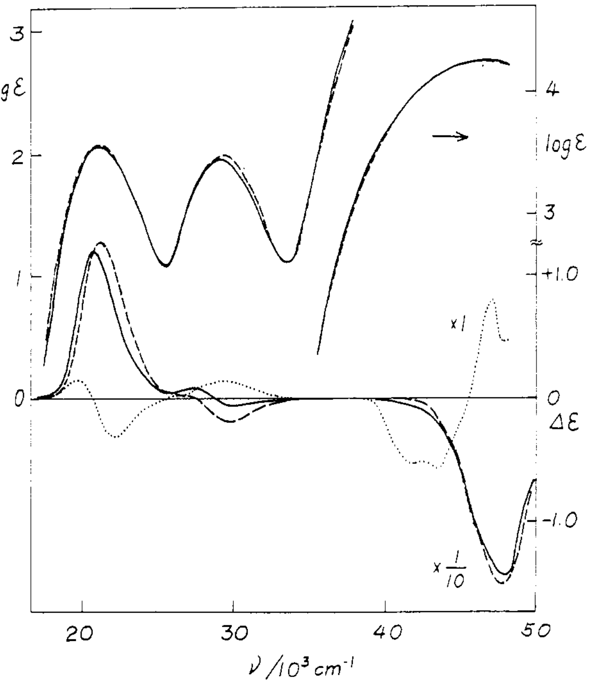

Figure 1. Absorption and CD spectra of Λ-*cis*-β-*SS*-$[Co(NH_3)_2(trien)]^{3+}$ (—) and Λ-*cis*-β-*SR*-$[Co(NH_3)_2(trien)]^{3+}$ (- -). The dotted line shows a DCD spectrum of both isomers (Λ-cis-β-SS − Λ-cis-β-SR).

The identification of cis-β isomers is consistent with a 5:3 formation ratio of the Λ-SS isomer to the Λ-SR isomer, which is a usual tendency observed for the trien complexes.[17,19] The results of strain-energy-minimization calculations also support this result (vide post).

As for the absolute configuration of the $(+)_{546}$- and $(-)_{546}$-*trans*-$[Co(NH_3)_2(trien)]^{3+}$ ion, a sector rule may be applied to this system.[20] Since the complex has a CoN_6 chromophore, its optical activity should correlate with the octahedral pseudoscalar;[20,21] i.e., *trans*-*SS*-$\delta\lambda\delta$-$[Co(NH_3)_2(trien)]^{3+}$ must exhibit mainly a negative Cotton effect with a minor positive band in the region

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Table II. Final Energy Terms (kJ mol^{-1}) for the Five Isomers of $[Co(NH_3)_2(trien)]^{3+}$

terms	Λ-cis-α	Λ-cis-β-*SS*	Λ-cis-β-*SR*	trans-*RR*	trans-*RS*
bond strain	2.8	3.4	3.5	4.2	3.8
nonbonded interactions	2.2	5.8	5.6	11.6	10.5
valence angle deformations	10.0	13.2	14.6	26.4	19.8
torsional interactions	23.2	18.4	19.2	16.3	23.7
total strain energy	38.2	40.8	42.9	58.4	57.8

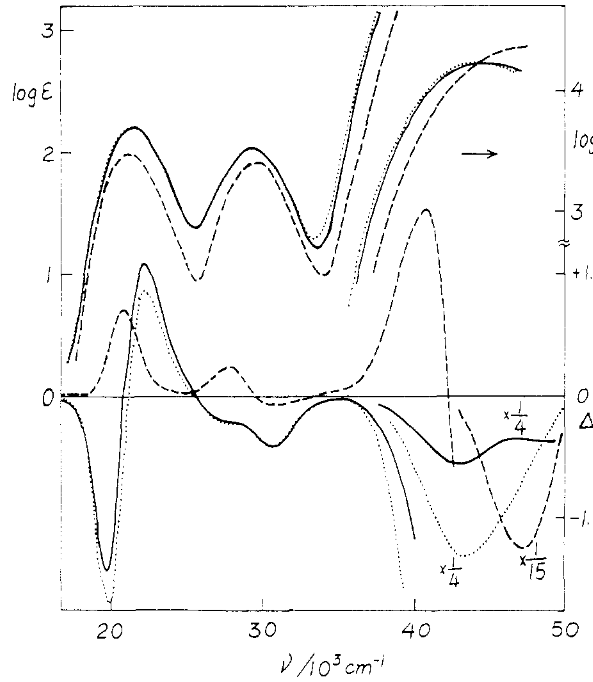

Figure 2. Absorption and CD spectra of $(+)_{546}$-*cis*-α-$[Co(NH_3)_2(trien)]^{3+}$ (--), $(-)_{546}$-*trans*-$[Co(NH_3)_2(trien)]^{3+}$ (—), and *trans-RR*-δλδ-$[Co(NH_3)_2(2,9\text{-dimetrien})]^{3+}$ (···).

of the $A_{1g} \rightarrow T_{1g}$ octahedral transition.[20,21] This is not the case, however. It is difficult to distinguish which is the major CD band in the spectrum of $(-)_{546}$-*trans*-$[Co(NH_3)_2(trien)]^{3+}$, as Figure 2 shows. Moreover, the Δε values of the first absorption band region are so large that they can not be compared with those of the complexes that Mason cited as examples being governed by the octahedral pseudoscalar.[21]

In order to clarify the absolute configuration of the trans isomers, a corresponding diammine complex was prepared with a ligand, (2*S*,9*S*)-2,9-dimethyl-1,4,7,10-tetraazadecane (2,9-dimetrien), which is expected to form only one trans isomer of the *RR*-δλδ conformation, due to its stereospecific coordination.[22] Figure 2 also shows its CD spectrum. The similarity of the CD spectra of both trans isomers is pronounced. The situation was also found in the spectra of *trans-SS*-$[CoCl_2(trien)]^+$ and the corresponding 3,8-dimetrien complex.[23] Since the methyl groups of these dimetrien complexes lie in or close to a CoN_4 (N_4 = tetraamine) plane, they may not strongly affect the optical activity of the complexes. Thus, $(-)_{546}$-*trans*-$[Co(NH_3)_2(trien)]^{3+}$ is concluded to possess the *SS*-δλδ conformation. This conclusion is supported by the fact that $(-)_{589}$-*trans-SS*-$[Co(NCS)_2(trien)]^{+}$[24] gave $(-)_{546}$-*trans*-$[Co(NH_3)_2(trien)]^{3+}$ by treatment with H_2O_2 in 0.1 M HCl at 40 °C.

It is interesting to note that the absolute configuration of optically active *trans*-$[Co(NH_3)_2(trien)]^{3+}$ can be deduced if the tetragonal pseudoscalar model is assumed to be applicable to this isomer instead of a more complicated rule derived from the octahedral pseudoscalar.[20,21] Since the present isomer can be treated as having the D_{4h} chromophore, the $A_{1g} \rightarrow E_g$ and the $A_{1g} \rightarrow A_{2g}$ transitions are expected to arise at 20970 and 22200 cm^{-1}, respectively.[25] The difference between the ligand field strength of the axial ligands (NH_3) and that of the planar ligand (trien) must be somewhat larger than that of, for example, *trans*-$[Co(NH_3)_2(N\text{-}CH_3\text{-}(+)\text{-}pn_2]^{3+}$, which was treated by the octahedral pseudoscalar model.[21] Then, if the tetragonal pseudoscalar model is applicable to *trans*-$[Co(NH_3)_2(trien)]^{3+}$, the $(-)_{546}$ isomer is assigned to the *SS* conformer, because the negative Cotton effect was observed at the longer wavelength CD maxima of the isomer. This is in accord with the assignment derived from the results of the stereospecific formation of *trans-RR*-δλδ-$[Co(NH_3)_2(2,9\text{-dimetrien})]^{3+}$.

The ^{13}C NMR spectra of the present isomers are already reported.[4] The spectra reflect the symmetry of each isomer. A striking similarity is found between these spectra and those of five isomers of $[Co(NCS)_2(trien)]ClO_4$.[6] This means that the coordination mode and the conformation of the trien moiety are mainly responsible for the chemical shifts of these ^{13}C NMR spectra.

Table II shows the result of the strain-energy-minimization calculation. The result shows that the cis-β-*SS* isomer is more stable than the cis-β-*SR* isomer. Since the isomerization of two cis-β isomers takes place without breaking of the metal-ligand bond, the synthetic formation ratio, 1.7, must be an equilibrium constant. The value is comparable to the calculated one.

The trans isomers have higher strain energies than the cis isomers. At these energy differences, the formation ratio of the trans to the cis isomers in equilibrium would be much less than 0.001. This must be related to the fact that they could not be obtained by the direct displacement of the unidentate ligand with ammonia.

The isomerization reaction was carried out with the trans-meso and the trans-*rac* isomers. They were easily isomerized to each other when the solution of each isomer was buffered to pH 5.8 with a mixture of 2,6-lutidine and HCl for 30 min. Although an appreciable extent of the hydrolysis reaction to liberate ammonia took place at the same time, the formation ratio obtained was 4:5 for meso:*rac*, regardless of the starting materials. The ratio is near to that estimated (5:4) from the calculated energy difference. The good correlations thus obtained between observed and calculated energy differences show that the present modified calculations are more reliable than those in the previous reports.[4,10]

Registry No. *cis*-α-$[Co(NH_3)_2(trien)](ClO_4)_3$, 69961-06-4; Λ-*cis*-β-*SS*-$[Co(NH_3)_2(trien)](ClO_4)_3$, 97074-07-2; Λ-*cis*-β-*SR*-$[Co(NH_3)_2(trien)](ClO_4)_3$, 97133-87-4; (+)-*trans-RR*-$[Co(NH_3)_2(trien)](ClO_4)_3$, 97168-84-8; *trans-RS*-$[Co(NH_3)_2(trien)](ClO_4)_3$, 75365-36-5; *cis*-α-$[CoCl_2(trien)]Cl$, 14883-58-0; *cis*-β-$[Co(NH_3)_2(trien)]^{3+}$, 48131-37-9; *trans*-$[Co(NCS)_2(trien)]ClO_4$, 97133-89-6; *rac-trans*-$[Co(NH_3)_2(trien)](ClO_4)_3$, 97133-91-0; *trans-SS*-$[Co(NH_3)_2(2,9\text{-dimetrien})](ClO_4)_3$, 97074-09-4; *trans-SS*-$[Co(NCS)_2(2,9\text{-dimetrien})]ClO_4$, 97074-11-8.

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(22) Due to the presence of a methyl group, the nitrogen chirality of this isomer is represented inversely to that of the corresponding trien complex of the same conformation.

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(25) These values are cited from the $A_{1g} \rightarrow T_{1g}$ transition of $[Co(NH_3)_6]^{3+}$ and the $A_{1g} \rightarrow E_g$ transition of *trans*-$[CoCl_2(trien)]^{+}$[23], by referring to the theoretical treatment. Yamatera, H. *Bull. Chem. Soc. Jpn.* **1958**, *31*, 95.