

1, 10-디벤질트리에틸렌테트라아민과 1, 10-디벤질-5R-
 메틸트리에틸렌테트라아민의 코발트(III) 착물

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Metal Complexes Containing Multidentate Ligands(I).
 Cobalt(III) Complexes of 1, 10-Dibenzyltriethylenetetraamine
 and 1, 10-Dibenzyl-5R-methyltriethylenetetraamine

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요약. 두개의 리간드 1, 10-디벤질트리에틸렌테트라아민 (1, 10-Be₂trien)과 1, 10-디벤질-5R-메틸트리에틸렌테트라아민 (1, 10-Be₂-5R-Metrien)을 합성하고 이들 두 리간드의 디클로로 코발트(III) 착물을 제조하였다. 이 두 테트라아민 리간드는 코발트(III) 이온에 대하여 트랜스 기하배위를 아주 잘 형성하였다.

Abstract. The synthesis of two new ligands, 1, 10-dibenzyltriethylenetetraamine(1, 10-Be₂trien) and 1, 10-dibenzyl-5R-methyltriethylenetetraamine(1, 10-Be₂-5R-Metrien), and the preparation of the dichloro cobalt(III) complexes of these ligands are reported. Both tetraamine ligands yield exclusively *trans* geometry upon coordination to the cobalt(III) ion.

Introduction

Cobalt(III) complexes with triethylenetetraamine (trien), and with derivatives of trien which have one or more substituents at the carbon atom (s) of the trien skeleton, have been observed to yield both *cis* and *trans* isomers¹⁻⁵(Fig. 1). However, when a methyl group was substituted at the terminal nitrogens of trien, cobalt(III) complexes with these ligands have been shown to form *trans* isomers exclusively⁶. Thus, the ligand, 1, 10-dimethyltriethylenetetraamine, which has a

methyl group at both terminal nitrogens, formed the *trans* complex only with the cobalt(III) ion.

In this paper we report the synthesis of new terminal N-substituted straight chain flexible tetraamine ligands, 1, 10-dibenzyltriethylenetetra-

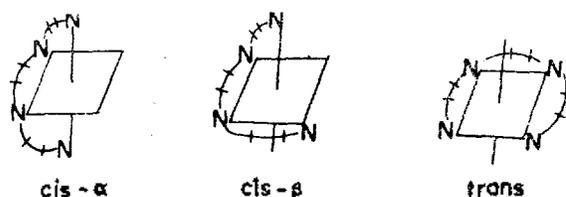


Fig. 1. Geometrical isomers of trien complex in octahedral structure.

(trien=H₂NCH₂CH₂NHCH₂CH₂NHCH₂CH₂NH₂)

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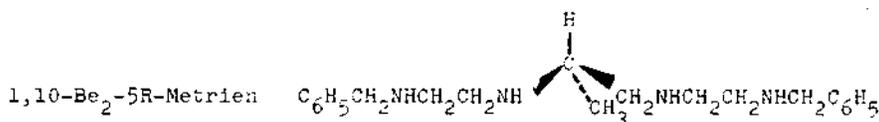
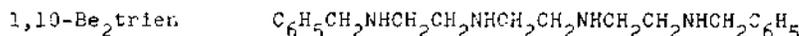


Fig. 2. The structure of ligands synthesized in this study.

aamine(1,10-Be₂trien) and 1,10-dibenzyl-5R⁷-methyltriethylenetetraamine(1,10-Be₂-5R-Metrien)(Fig. 2), and the preparation of dichloro cobalt(III) complexes with these ligands. The outstanding feature of these ligands is the benzyl substituent at the terminal nitrogen atoms of the trien skeleton. Because of the size and bulky nature of this substituent, it was expected that these two ligands would show strong preference for the *trans* geometry when they coordinated to the cobalt(III) ion.

Experimental Section

Chemical Reagents. The propylenediamine and benzyl amine were purchased from Aldrich Chemical Co., Milwaukee, Wisconsin, U. S. A., and the lithium aluminum hydride from Ventron Corp., Beverly, Mass., U. S. A. All other chemicals used were commercial reagent grade.

Physical Measurements. The infrared spectra of the solid samples were recorded using potassium bromide disks on a Perkin-Elmer Model 337 Grating Spectrophotometer. The spectra of liquid samples were taken of neat smears on KBr plates. The electronic absorption spectra were obtained using a Unicam SP 800A UV Spectrophotometer. The ORD and CD curves were measured on a Jasco ORD/CD-5 Spectrophotometer using 1-cm cell and using water as the solvent. The pmr spectra were obtained using a Varian A-60 Spectrometer, and using 2,2-dimethyl-2-silapentane-5-sulfonate(DSS) as an internal standard. The

solvent was D₂O. Elemental analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Michigan, U. S. A. and by Micro-Tech Laboratories, Skokie, Illinois, U. S. A.

Preparation of *N,N'*-Bis(chloroacetyl)-ethylenediamine. This was prepared according to the method of Yoshikawa, *et al.*⁶, m. p 174~175°C.

Preparation of *N,N'*-Bis(*N*-benzylglycyl)-ethylenediamine Dihydrochloride. 14.0 g of dried and pulverized *N,N'*-bis(chloroacetyl)-ethylenediamine was added to a mixture of methanol(300 ml) and 40 % benzylamine aqueous solution(400 g). The reaction mixture was allowed to stand for one week, and then was concentrated until no more evaporation occurred. When ether was added to the concentrated mixture, white crystals precipitated. The white product was collected by filtration and dried in the air. Yield 17.2 g.

Preparation of 1,10-Dibenzyltriethylenetetraamine Tetrahydrochloride(1,10-Be₂trien). 300 ml of anhydrous tetrahydrofuran and 10.0 g of lithium aluminum hydride were placed in a one-liter three-necked round bottom flask equipped with a mechanical stirrer and a reflux condenser in an ice bath. Then 13.1 g of dried and pulverized *N,N'*-bis(*N*-benzylglycyl)-ethylenediamine dihydrochloride was added with vigorous stirring in an ice bath. After stirring at room temperature for 30 min, the reaction mixture was refluxed and stirred for 24 hours. The reaction mixture was cooled in an ice bath, and a solution of 20 g

of water and 250 ml of tetrahydrofuran was cautiously added with vigorous stirring. The solid mixture was filtered off and the filtered cake was extracted twice with boiling tetrahydrofuran. The combined tetrahydrofuran was concentrated under reduced pressure to give a pale yellow oil. The oil was dissolved in absolute ethanol and concentrated hydrochloric acid was added. The precipitated white crystals were removed by filtration, washed with absolute ethanol, and recrystallized from water and ethanol.

Anal. Calc'd. for $C_{20}H_{30}N_3 \cdot 4HCl$: C, 50.86; H, 7.26; N, 11.86. Found: C, 51.22; H, 7.59; N, 11.74.

Resolution of *R, S*-Propylenediamine. To get *R*-propylenediamine *R, S*-propylenediamine was resolved according to the method of Dwyer, *et al.*⁸ using *d*-tartaric acid. The least soluble diastereoisomer contained the levo propylenediamine. After twelve recrystallizations the diastereoisomer was converted to the dihydrochloride by the method of Bailar, *et al.*⁹. The levo base was obtained by cautious distillation of the hydrochloride mixed with an excess of sodium hydroxide.

Preparation of *N, N'*-Bis(chloroacetyl)-*R*-Propylenediamine. This was prepared according to the method of Yoshikawa, *et al.*¹⁰

Preparation of *N, N'*-Bis(*N*-benzylglycyl)-*R*-propylenediamine Dihydrochloride. 18.0 g of dried and pulverized *N, N'*-bis(chloroacetyl)-*R*-propylenediamine was added to a mixture of methanol(300 ml) and 40 % benzylamine aqueous solution(400 g). The reaction mixture was allowed to stand for 9 days, and then was concentrated under reduced pressure. When ether was added to the concentrated solution, white crystals precipitated. The white product was removed by filtration and dried in the air. Yield 21.4g.

Preparation of 1, 10-Dibenzyl-5*R*-methyltriethylenetetraamine Tetrahydrochloride(1, 10-*Be*₂-5*R*-Metrien·4HCl). 250 ml of anhydrous

tetrahydrofuran and 9.5 g of lithium aluminum hydride were placed in a 1000 ml three necked round bottom flask equipped with a mechanical stirrer and a reflux condenser in an ice bath. Then 18.0 g of *N, N'*-bis(*N*-benzylglycyl)-*R*-propylenediamine dihydrochloride was carefully added with vigorous stirring. After stirring at room temperature for 30 min., the reaction mixture was refluxed and stirred for 24 hours. The reaction mixture was cooled in an ice-salt bath, and a solution of 19 g of water and 250 ml of tetrahydrofuran was carefully added with vigorous stirring. The solids were filtered off and the filtered cake was extracted twice with boiling tetrahydrofuran. The combined tetrahydrofuran filtrate and washings were concentrated under reduced pressure to give a pale yellow oil. The oil was dissolved in absolute ethanol and concentrated hydrochloric acid was added. The precipitated white crystals were removed by filtration, washed with absolute ethanol several times, and recrystallized from water and ethanol.

Anal. Calc'd. for $C_{21}H_{32}N_4 \cdot 4HCl$: C, 51.86; H, 7.46; N, 11.52. Found: C, 51.55; H, 7.61; N, 11.60.

Preparation of *Trans*-(Co(1, 10-*Be*₂trien)-Cl₂)ClO₄. 2.36g(0.005 mole) of 1, 10-dibenzyltriethylenetetraamine tetrahydrochloride (1, 10-*Be*₂trien·4HCl) was dissolved in 200 ml of ethanol-water solution(1:1 ratio by volume). 1.19 g (0.005 mol) of CoCl₂·6H₂O dissolved in 50 ml of water was added to the above mentioned solution, which was followed by the addition of 0.8 g of LiOH·H₂O. The resultant solution was aerated with CO₂-free air for 30 hours. The solution was evaporated under moving air at room temperature to one-fifth its original volume. Then 5.0 ml of concentrated hydrochloric acid was added and evaporation continued until the volume was less than 15 ml. The solution was cooled to 0 °C. When excess of LiClO₃·3H₂O was added, green

crystals precipitated. The product was filtered and washed with acetone, and dried under vacuum. Yield 0.18 g.

Anal. Calcd. for $\text{CoC}_{20}\text{H}_{30}\text{N}_4\text{Cl}_3\text{O}_4$: C, 43.22; H, 5.44; N, 10.08. Found: C, 43.29; H, 5.36; N, 9.98.

Preparation of *Trans*-(Co(1, 10-Be₂-5R-Metrien)Cl₂)ClO₄. This was prepared by the same

method as that used for *trans*-(Co(1, 10-Be₂-trien)Cl₂)ClO₃ using 2.43 g of 1, 10-Be₂-5R-Metrien·4HCl in place of 1, 10-Be₂-trien·4HCl. Yield 0.21 g.

Anal. Calc'd. for $\text{CoC}_{21}\text{H}_{32}\text{N}_4\text{Cl}_3\text{O}_4$: C, 44.27; H, 5.66; N, 9.83. Found: C, 43.98; H, 5.61; N, 9.79.

Results and Discussion

Preparation. The ligands, 1, 10-Be₂-trien and 1, 10-Be₂-5R-Metrien have been prepared following the known synthetic route⁶. The pmr spectrum of 1, 10-Be₂-trien is shown in Fig. 3a. The singlet farthest downfield (δ 7.43) represents the aromatic protons, and the benzylic methylene protons resonate at δ 4.30. The pmr chemical shift pattern of this compound is consistent with the structural assignment. The other two peaks at about δ 3.4 with the integration ratio two to one indicate the remaining ethylene protons of the

trien skeleton. The pmr spectrum of 1, 10-Be₂-5R-Metrien has shown a somewhat similar chemical shift pattern as that of 1, 10-Be₂-trien with a doublet at about δ 1.55 (Fig. 3b) corresponding to the methyl protons.

The dichloro cobalt(III) complexes of 1, 10-Be₂-trien and 1, 10-Be₂-5R-Metrien have been prepared by the general technique of air oxidation of an aqueous mixture of cobalt(II) chloride, LiOH·H₂O, and the ligand followed by acidification with the concentrated hydrochloric acid. Both complexes have been obtained as light green crystals, which suggest that the compounds obtained have the *trans* configuration, since all the known *trans* dichloro cobalt(III) complexes of tetraamine ligands have been found to be green in color.¹⁻⁶

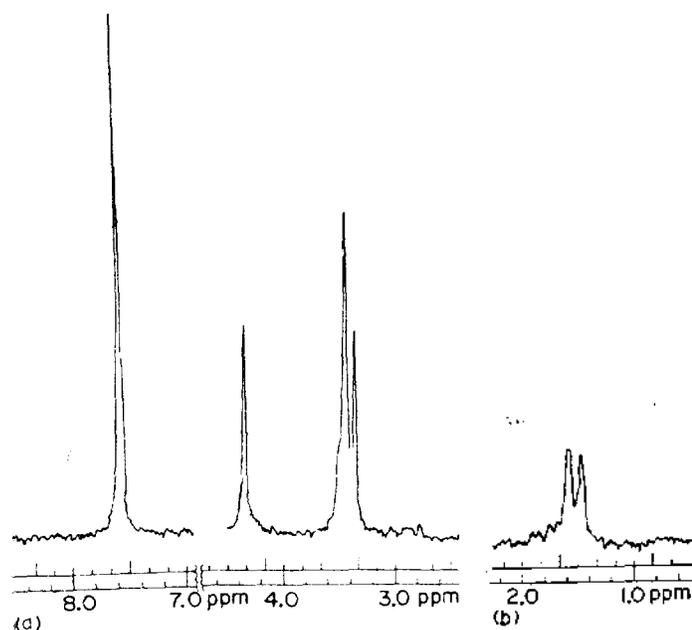


Fig. 3. pmr spectra of: (a) 1, 10-Be₂-trien·4HCl in D₂O and (b) 1, 10-Be₂-5R-Metrien·4HCl in D₂O shown above δ 2.0 only.

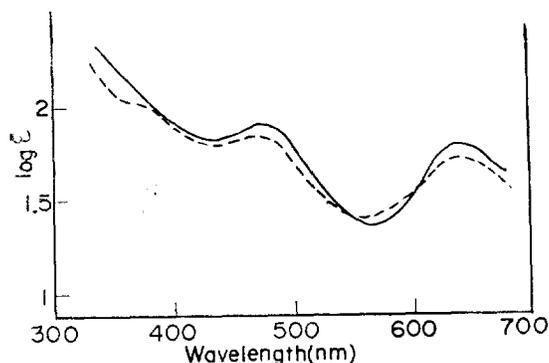


Fig. 4. Electronic absorption spectra of *trans*-(Co(1, 10-Be₂-trien)Cl₂)⁺ (—) and *trans*-(Co(1, 10-Be₂-5R-Metrien)Cl₂)⁺ (.....).

No other isomers have been isolated in this preparation.

Electronic Absorption Spectra. Electronic absorption spectra for *trans*-[Co(1,10-Be₂trien)Cl₂]⁺ and *trans*-[Co(1,10-Be₂-5R-Metrien)Cl₂]⁺ are shown in Fig. 4. Both spectra show split bands in the long wavelength region where the *cis* configuration would show a broad band. Therefore, these complexes have been assigned the *trans* configuration on the basis of their visible spectra. For the complexes of the type *trans*-CoN₄Cl₂⁺ the ¹T₁(O_h) state is split into ¹E and ¹A₂ components and, according to the Yamatera's theory,¹¹ the ¹A₁→¹E transition occurs at a lower energy than the ¹A₁→¹A₂ transition. This theory has been supported by the polarized spectra of crystals of *trans*-[Co(en)₂Cl₂]Cl·HCl·2H₂O along, and perpendicular to, the Cl—Co—Cl axis. The spectra show that the long wavelength band (*I_a* band) at 625 nm is the ¹A₁→¹E(*D_{4h}*) transition and the next shorter wavelength band (*I_b* band) at 455 nm is the ¹A₁→¹A₂(*D_{4h}*) transition¹². The *trans* dichloro cobalt(III) complexes of trien³ and substituted trien ligands^{1,2,4-6} show this pattern (*I_a* band in the range of 630~640 nm and *I_b* band 470~485 nm), and the same assignments of transition have been applied.

The electronic absorption spectra of the dichloro cobalt(III) complexes of 1,10-Be₂trien and 1,10-Be₂-5R-Metrien (Fig. 4) also show this pattern with the splitting of the first absorption band in the visible region as expected for the *trans* complexes. The first absorption (¹A₁→¹T₁ in O_h) is generally observed in these complexes at about 635nm (*I_a* band) and about 480 nm (*I_b* band). From the comparison of the visible spectra of these complexes with those of known complexes, it is clear that the complexes prepared in this study have the *trans* configuration.

Fig. 5 shows three possible isomers of the *trans* 1,10-Be₂trien complex with the terminal *N*-benzyl

groups in the equatorial position. The *RR* and *SS* isomers have three gauche ring conformations due to the configurations about the secondary nitrogen atoms in the central chelate ring. Other structures, in which the terminal *N*-benzyl groups are axial, should be energetically unstable. No attempt was made to resolve this complex in this work.

Circular Dichroism Spectrum. The CD spectra of *trans*-[Co(tetraamine)Cl₂]⁺ ions with *SS*-3,8-Me₂trien and with other trien ligands having methyl substitution at the terminal nitrogens—*R*-1,5,10-Me₃trien, *SS*-1,2,9,10-Me₄trien, and *SS*-1,3,8,10-Me₄trien—have been reported by Yoshikawa and coworkers.^{6,11} All of the complex ions showed similar CD spectra in the region of 570~680 nm (*I_a* absorption band region). In this region these complexes have a dominant negative CD band followed by a less significant positive band. Based upon these observations it has been shown that these complexes have a δ¹² ring conformation in their outside chelate rings and λ¹² ring conformation in their central chelate ring. The assignment of these ring conformations has recently been confirmed by an X-ray crystallographic study.¹³

The *trans* dichloro cobalt(III) complex of *SS*-3,8-Me₂trien has a positive CD band at about 460 nm (*I_b* absorption band region), which is ascribed to the ¹A₁→¹A₂(*D_{4h}*) electronic transition. In contrast, the *trans* dichloro cobalt(III) complexes of other trien ligands with methyl substitution at the ter-

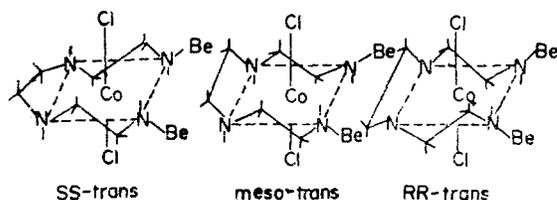


Fig. 5. Possible structures of *trans*-[Co(1,10-Be₂trien)Cl₂]⁺ ion with benzyl group in equatorial position. (Be=benzyl group)

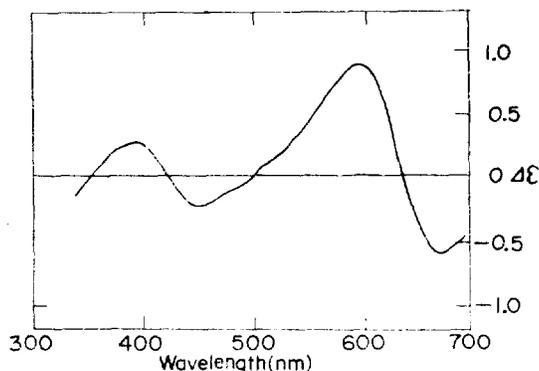


Fig. 6. Circular dichroism spectrum of *trans*-(Co(1,10-Be₂-5R-Metrien)Cl₂)⁺ ion.

minal nitrogens have a CD band in this region whose sign is opposite that of *trans*-(Co(SS-3,8-Me₂trien)Cl₂)⁺. This difference has been explained by means of the vicinal effect from the *R*-asymmetric nitrogen caused by the methyl substituent at the terminal nitrogen centers.⁶

The second ligand synthesized in this work, 1,10-Be₂-5R-Metrien, contains an asymmetric carbon center. The CD curve of the *trans* dichloro cobalt(III) complex of this ligand (Fig. 6) has a negative CD band followed by a positive band in the region of 570~680 nm and a negative CD band at about 460 nm. This is similar to the *trans* dichloro cobalt(III) complexes of *R*-1,5,10-Me₃-trien⁶ and other trien ligands with methyl substitution at the terminal nitrogens.⁶ By comparing the major CD band in the ¹A₁→¹E electronic transition of the *trans*-(Co(1,10-Be₂-5R-Metrien)Cl₂)⁺ ion with those of other *trans*-(Co(tetraamine)Cl₂)⁺ ions^{6,11} it is concluded that they have the same chelate ring conformations: λ for the central chelate ring and δ for the two outside chelate rings. The negative CD band at about 460 nm should be the contribution from the *R*-

asymmetric nitrogen centers caused by the introduction of a benzyl group at each terminal nitrogen. The benzyl group of the 1,10-Be₂-5R-Metrien should take the equatorial position upon coordination to the cobalt(III) ion and imparts *R*-asymmetry at the terminal nitrogens. Both nitrogens in the central chelate ring should have the *S* absolute configuration. Therefore, the overall configuration of this complex is *trans*-(*RSSR*) with the δλδ chelate ring conformation.

References

1. R.G. Asperger and C.F. Liu, *Inorg. Chem.* **4**, 1935(1965).
2. R.G. Asperger, *ibid.*, **8**, 2127(1969).
3. A.M. Sargeson and G.H. Searle, *ibid.*, **4**, 45 (1965); *ibid.*, **6**, 787(1967).
4. M. Saburi and S. Yoshikawa, *Bull. Chem. Soc. Japan*, **45**, 806(1972).
5. M. Goto, H. Matsushita, M. Saburi and S. Yoshikawa, *Inorg. Chem.*, **12**, 1498(1973.)
6. M. Goto, A. Okubo, T. Sawai and S. Yoshikawa, *ibid.*, **9**, 1488(1970).
7. R and S nomenclature by R.S. Cahn, C.K. Ingold and V. Prelog, *Angew. Chem. Intern. Edn.*, **5**, 385(1966).
8. F.P. Dwyer, F.L. Garvan and A. Shulman, *J. Amer. Chem. Soc.*, **81**, 290(1959).
9. J.C. Bailar, H.B. Johnson and A.D. Gott, *ibid.*, **74**, 3131(1952).
10. M. Goto, M. Saburi, and S. Yoshikawa, *Inorg. Chem.*, **8**, 358(1969).
11. S. Yoshikawa, T. Sekihara and M. Goto, *ibid.*, **6**, 169(1967).
12. *Inorganic Chemistry*, **9**, 1(1970).
13. M. Ito, F. Marumo and Y. Saito, *Acta Cryst.*, **B28**, 463(1972).