

여러자리 리간드의 금속착물 (제 2 보).
1, 10-디프로필-5R-메틸트리에틸렌테트라아민의 디클로로
및 디니트로 코발트(III) 착물

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Metal Complexes Containing Multidentate Ligands (II).
Dichloro and Dinitro Cobalt(III) Complexes of 1, 10-Dipropyl-
5R-methyltriethylenetetraamine*

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요 약. 새로운 네자리 아민리간드 1, 10-dipropyl-5R-methyltriethylenetetraamine(R-Pr₂metrien)이 합성되었고 이 리간드로부터 디클로로 및 디니트로코발트(III) 착물이 합성되었다. 합성된 리간드는 트랜스 이성체의 착물만을 형성할 것이 예측되었으며 예측된대로 트랜스 이성체만을 형성하였다. 원소분석, 핵자기공명분광학, 흡수분광분석 및 원편광이색성분광법을 이용하여 리간드와 착물의 구조가 설명되었다.

ABSTRACT. A straight chain flexible tetraamine ligand, 1, 10-dipropyl-5R-methyltriethylenetetraamine(R-Pr₂metrien) has been synthesized, and the dichloro and dinitro cobalt(III) complexes of this ligand have been prepared. The ligand has been expected to show a topological preference for the *trans* isomer. As expected, only *trans* geometrical isomers have been obtained and their structures have been elucidated via elemental analyses, nmr, electronic absorption and CD data.

INTRODUCTION

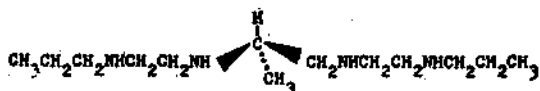
Cobalt (III) complexes with triethylenetetraamine(trien) and those with derivatives of

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* isomers.¹ However, when a methyl or benzy group was substituted at the terminal nitrogen atoms of trien, the cobalt(III) complexes of those

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ligands have been shown to form *trans* isomers exclusively.^{2,3}

In this paper we report the synthesis of a straight chain tetraamine ligand, 1,10-dipropyl-5*R*-methyltriethylenetetraamine (R-Pr₂ metrien), and the preparation of both the dichloro and the dinitro cobalt(III) complexes of this ligand. The outstanding feature of this ligand is that it has not only one asymmetric carbon center but also one propyl substituent at each terminal nitrogen atom which becomes asymmetric upon coordination of the ligand to the cobalt(III) ion. Although the propyl group is bulkier than the methyl group, it is less bulkier than the benzyl group. Therefore, the ligand has also been expected to show a topological preference for the *trans* isomer. The structure and absolute configuration of the ligand prepared in this work is shown below.



EXPERIMENTAL

The ir and uv-visible spectra were obtained using a Perkin-Elmer Model 337 Grating Spectrophotometer and a Unicam SP 800A UV spectrophotometer, respectively. The CD curves were measured on a Jasco ORD/CD-5 Spectrophotometer. The pmr spectra were recorded using a Varian A-60 Spectrometer (DDS for the internal standard and D₂O for the solvent). Elemental analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Michigan. All the spectra for the dichloro complex were taken the color of the water solution remained green.

Resolution of Propylenediamine. Propylenediamine was resolved according to the method of Dwyer, *et al.*⁴ using the d-tartaric acid.

The diastereomer was converted to the dihydrochloride by the method of Bailar, *et al.*⁵ The levo base was obtained by cautious distillation of the hydrochloride mixed with an excess of sodium hydroxide.

N, N'-bis (N-Propylglycyl)-R-propylenediamine Dihydrochloride. A powdered sample of N, N'-bis(chloroacetyl)-R-propylenediamine⁶ (34.2g) was added to a mixture of methanol (300 ml) and 40% propylamine aqueous solution (300 g). The reaction mixture was allowed to stand for one week at room temperature. The mixture was then evaporated to dryness under reduced pressure. The product was recrystallized from ethanol. Yield 40.1 g.

Anal. Calcd. for C₁₃H₂₈O₂N₄·2HCl: C, 45.22; H, 8.76; N, 16.22.

Found: C, 45.19; H, 8.22; N, 16.23.

1,10-Dipropyl-5*R*-methyltriethylenetetraamine Tetrahydrochloride (R-Pr₂ metrien·4HCl). 500 ml of anhydrous tetrahydrofuran and 18.1 g of lithium aluminum hydride were placed in a one-liter three-necked round bottom flask equipped with a mechanical stirrer and reflux condenser in an ice bath. Then 35.0 g of N, N'-bis (N-propylglycyl)-R-propylenediamine dihydrochloride was added cautiously. The reaction mixture was refluxed and stirred for 24 hrs. The reaction mixture was cooled in an ice bath, and a solution of 35.0 g of water and 300 ml of THF was cautiously added. The mixture was filtered off and the solid part was extracted twice with boiling THF. The combined THF was concentrated under reduced pressure to give a pale yellow oil. The oil was dissolved in absolute ethanol and HCl was added. The precipitated white product was collected by filtration, and washed with ethanol and ether. Yield 16.2 g.

Anal. Calcd. for C₁₃H₃₂N₄·4HCl: C, 40.00; H, 9.30; N, 14.36.

Found: C, 39.96; H, 9.33; N, 14.33.

trans-[Co(R-Pr₂ metrien) Cl₂] ClO₄·3.90g of R-pr₂ metrien·4HCl and 1.52g of LiOH·H₂O were dissolved in 100 ml of water, which was followed by the addition of 2.38g of CoCl₂·6H₂O dissolved in 50ml of water. The brown solution was aerated with CO₂-free air for 24 hrs. The solution was evaporated under moving air at room temperature to one-fifth its original volume. 5.0ml of conc HCl was added and the evaporation continued until the volume was less than 15ml. The solution was cooled to 5°C. When excess LiClO₄·3H₂O was added, green crystals precipitated. The product was filtered off, washed with acetone, and dried under vacuum. Yield 0.52g.

Anal. Calcd for [Co(C₁₃H₃₂N₄)Cl₂]ClO₄: C, 32.96; H, 6.81; N, 11.83. Found: C, 32.91; H, 6.80; N, 11.80.

trans-[Co(R-Pr₂ metrien)(NO₂)₂]ClO₄. To a solution of 3.90 g of R-Pr₂metrien·4HCl and 1.46 g of LiOH·H₂O dissolved in 100 ml of water were added 2.38 g of CoCl₂·6H₂O and 1.38 g of NaNO₂. The solution was aerated with CO₂-free air at room temperature for 24 hrs. The solution was evaporated on a steam bath to less than 15 ml, excess LiClO₄·3H₂O was added, and then stored in a refrigerator overnight. The precipitated crystals were filtered and washed with acetone, ethanol, and ether: Yield 2.44 g.

Anal. Calcd for [Co(C₁₃H₃₂N₄)(NO₂)₂]ClO₄: C, 31.56; H, 6.52; N, 16.98.

Found: C, 31.51; H, 6.50; N, 16.97.

RESULTS AND DISCUSSION

The pmr spectrum of the ligand, R-Pr₂metrien·4HCl (*Fig. 1*), shows the methylene protons between nitrogen atoms at δ (3.25), the middle methylene protons in the propyl group at δ (2.16) and the other methylene protons in

the propyl group at δ (3.43). The methyl protons in the propyl group and the methyl protons on the asymmetric carbon atom resonate between δ (1.35) and δ (1.60). The dichloro complex has been obtained as a green compound, which suggests that the complex has the *trans* geometry.^{1-3, 6-8} On the basis of the electronic absorption spectra (*Fig. 2*), both the dichloro and the dinitro complexes have been assigned the *trans* geometry^{2, 7-10}. No other isomers were isolated in this preparation.

The CD spectra of *trans*-[Co(tetraamine)Cl₂]⁺ ions with SS-3, 8-me₂trien¹¹ and with trien ligands having the methyl or benzyl substitution at the terminal nitrogens—R-1, 5, 10-me₃trien², SS-1, 3, 8, 10-me₄-trien², and 1, 10-Be₂-5R-metrien³—have been reported. All the complex ions show similar CD spectra in the region of 570~680 nm (*I_a* band region) with a dominant negative CD band followed by a positive band, and have been assigned the δ and λ ¹² ring conformation, respectively, in their two outside chelate rings and in their central chelate ring, which have recently been confirmed by an X-ray crystallographic study¹³. The negative CD band in the *I_b* band region (~460 nm) for the *trans*-1, 3, 8, 10-me₄ trien complex has been explained, in comparison with *trans*-[Co(SS-3, 8-me₂trien)Cl₂]⁺ ion, by means of the vicinal effect from the R asymmetric nitrogen caused by the methyl or benzyl substitution at the terminal nitrogen centers.^{2, 3}

The CD curve of the *trans*-[Co(R-Pr₂metrien)Cl₂]⁺ synthesized in this work shows a negative band followed by a positive band in the region of 570~680 nm and a negative band at about 460nm (*Fig. 1*) which are similar to the *trans* dichloro cobalt(III) complexes of R-1, 5, 10-me₂trien and other terminal N-substituted trienligands.^{2, 3} By comparing the major CD band in the ¹A₁→¹E(*D_{4h}*) electronic transition

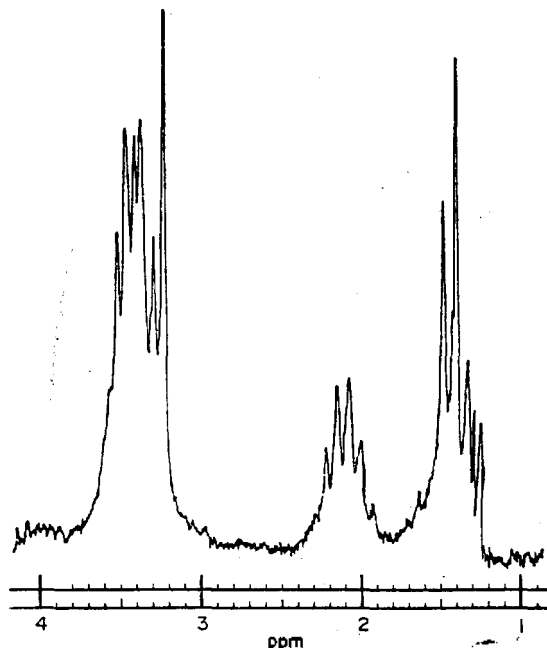


Fig. 1. pmr Spectrum of 1,10-Pr₂metrien·4HCl in D₂O.

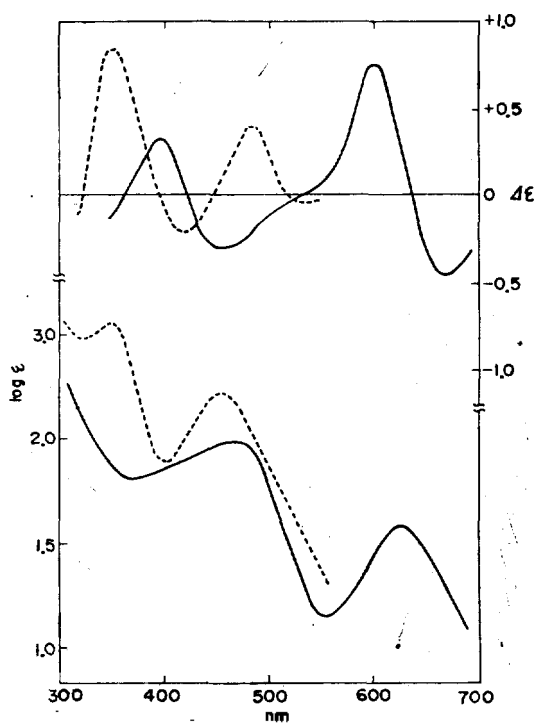


Fig. 2. Electronic absorption and circular dichroism spectra for *trans*-[Co(R-Pr₂metrien)Cl₂]⁺ (—) and for *trans*-[Co(R-Pr₂metrien)(NO₂)₂]⁺ (.....).

of the *trans*-[Co(R-Pr₂metrien)Cl₂]⁺ with that of other *trans*-[Co(tetraamine)Cl₂]⁺ ions,^{2,3} it is believed that they have the same chelate ring conformations: λ for the central ring and δ for the two outside chelate rings. The negative CD band at about 460nm should be the contribution from the R-asymmetric centers caused by the introduction of a propyl group at each terminal nitrogen atom. The propyl group should take the equatorial position upon coordination to the cobalt(III) ion and imparts R-asymmetry at the terminal nitrogen atoms.

From the study of the dinitro complexes of *trans*-[Co(SS-1, 3, 8, 10-me₄trien)(NO₂)₂]⁺ and *trans*-[Co(SS-3, 8-me₄trien)(NO₂)₂]⁺, which have the opposite CD bands in the visible-UV region, Yoshikawa, *et al.*² have shown that, in the case of dinitro complexes with the asymmetric nitrogen centers, the sign of the CD bands are essentially determined by the vicinal effect from the R-asymmetry by the methyl-substitution at the terminal atoms rather than by the chirality of the chelate ring, and that the signs of the Cotton effects induced from the R-asymmetric nitrogen are different for the corresponding component of the *trans*-[CoN₄Cl₂]⁺ and [*trans*-CoN₄(NO₂)₂]⁺ chromophores. The CD curve of *trans*-[Co(R-pr₂metrien)(NO₂)₂]⁺ resembles not that of *trans*-[Co(SS-3, 8-me₂trien)(NO₂)₂]⁺ but that of both *trans*-[Co(SS-1, 3, 8, 10-me₄trien)(NO₂)₂]⁺ and *trans*-[Co(R-1, 5, 10-me₃trien)(NO₂)₂]⁺ ions.² Therefore, it is believed that the R-asymmetry imparted at the terminal nitrogen atoms upon coordination by the propyl group should be mainly responsible for the shape of the CD curve observed.

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