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## Cobalt (III) Complexes with (R) - 1, 2-Diaminopropane and Its Derivatives

Christopher John Rudy

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COBALT(III) COMPLEXES WITH (R)-1,2-DIAMINOPROPANE  
AND ITS DERIVATIVES

by

Christopher John Rudy

A Thesis  
Submitted to the  
Faculty of The Graduate College  
in partial fulfillment of the  
requirements for the  
Degree of Master of Arts  
Department of Chemistry

Western Michigan University  
Kalamazoo, Michigan  
December 1985

COBALT(III) COMPLEXES WITH (R)-1,2-DIAMINOPROPANE  
AND ITS DERIVATIVES

Christopher John Rudy, M.A.

Western Michigan University, 1985

(R)-1,2-Diethylaminopropane (N,N'-Et1pn) was prepared by  $\text{LiAlH}_4$  reduction of (R)-1,2-diacetamidopropane (m.p.  $153.5^\circ\text{C}$ ). The  $[\alpha]_D$  of N,N'-Melpn and N,N'-Et1pn was related to that of 1pn and was concentration dependent. (R)-1,2-Dibenzylaminopropane was prepared. Complexes of trans,trans- and trans,cis-dinitrobis((R)-1,2-diethylaminopropane)cobalt(III) were prepared. The hexadecadal rule was used to help assign the nitro oxygens of the complexes to sectors adjacent to the axial amine hydrogens and within the boundaries of the  $\lambda$ -chelate rings. The CD spectra was solvent dependent. The instability of trans- $[\text{Co(III)}\text{N}_4\text{X}_2]^+$  complexes was related to the ammonia or 1,2-diamine ligand (N,N'-Bz1pn > N,N'-Et1pn > N,N'-Eten > N,N'-Melpn > N,N'-Meen >  $\text{NH}_3$  > 1pn), the trans-X groups ( $\text{Cl}^- > \text{Br}^- > \text{NO}_2^-$ ) and the counterion ( $\text{Cl}^- > \text{Br}^-; \text{ClO}_4^-; \text{NO}_3^-$ ).  $\text{NH}_4[\text{Co(III)}-(\text{NH}_3)_2(1,2\text{-diamine})(\text{SO}_3)_2]$  complexes were prepared, and trans- $[\text{Co(III)}(\text{NH}_3)_2(1\text{pn})\text{Br}_2]\text{Br}$  and trans- $[\text{Co(III)}(\text{NH}_3)_2(1\text{pn})\text{Cl}_2]\text{Cl}$  were prepared from  $\text{NH}_4[\text{Co(III)}(\text{NH}_3)_2(1\text{pn})-(\text{SO}_3)_2]$  using HBr or HCl.

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Christopher John Rudy

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*Western Michigan University*

**M.A. 1985**

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## DIAMINE ABBREVIATIONS

Diamine	Abbreviation
1,2-diaminoethane	en
1-methylamino-2-aminoethane	N-Meen
1-(methylethyl)amino-2-aminoethane	N-isopropylen
1,2-dimethylaminoethane	N,N'-Meen
1,2-diethylaminoethane	N,N'-Eten
1,2-dialkylaminoethanes	N,N'-Alkylen
1,2-diaminopropane (racemic)	pn
(R)-1,2-diaminopropane	l <sub>pn</sub>
(R)-1,2-dimethylaminopropane	N,N'-Mel <sub>pn</sub>
(R)-1,2-diethylaminopropane	N,N'-Etl <sub>pn</sub>
(R)-1,2-dibenzylaminopropane	N,N'-Bzl <sub>pn</sub>
(S)-1,2-diaminopropane	d <sub>pn</sub>
(S)-1-methylamino-2-aminopropane	N-Med <sub>pn</sub>
(S)-1-amino-2-methylaminopropane	N'-Med <sub>pn</sub>
(S)-1,2-dimethylaminopropane	N,N'-Med <sub>pn</sub>
1,3-diaminopropane	tn

# NEW COMPOUNDS PREPARED

---

## Compound

---

(R)-1,2-diethylaminopropane

(R)-1,2-dibenzylaminopropane

$[\text{Co(III)}(\text{N,N'-Et1pn})_2(\text{NO}_2)_2]^+$

trans,trans- $[\text{Co(III)}(\text{N,N'-Et1pn})_2(\text{NO}_2)_2]^+$

trans,cis- $[\text{Co(III)}(\text{N,N'-Et1pn})_2(\text{NO}_2)_2]^+$

trans- $[\text{Co(III)}(\text{N,N'-Et1pn})_2\text{Cl}_2]^+$  in situ

$[\text{Co(III)}(\text{N,N'-Eten})_2(\text{NO}_2)_2]^+$

$[\text{Co(III)}(\text{N,N'-Meen})_2\text{NO}_2\text{Cl}]\text{ClO}_4$

$[\text{Co(III)}(\text{N,N'-Eten})_2\text{NO}_2\text{Cl}]\text{ClO}_4$

$\text{NH}_4[\text{Co(III)}(\text{NH}_3)_2(\text{N,N'-Meen})(\text{SO}_3)_2]$

$\text{NH}_4[\text{Co(III)}(\text{NH}_3)_2(\text{N,N'-Me1pn})(\text{SO}_3)_2]$

$\text{NH}_4[\text{Co(III)}(\text{NH}_3)_2(\text{N,N'-Eten})(\text{SO}_3)_2]$

$\text{NH}_4[\text{Co(III)}(\text{NH}_3)_2(\text{N,N'-Et1pn})(\text{SO}_3)_2]$

$\text{NH}_4[\text{Co(III)}(\text{NH}_3)_2(\text{N,N'-Bz1pn})(\text{SO}_3)_2]$

trans- $[\text{Co(III)}(\text{NH}_3)_2(\text{1pn})\text{Cl}_2]\text{Cl}$

trans- $[\text{Co(III)}(\text{NH}_3)_2(\text{N,N'-Meen})\text{Cl}_2]\text{Cl}$

NEW OR IMPROVED METHODS TO KNOWN COMPOUNDS

---

Compound Prepared

---

(R)-1,2-diaminopropane

1,2-dimethylaminopropane

trans-[Co(III)(NH<sub>3</sub>)<sub>2</sub>(1pn)Br<sub>2</sub>]Br



# KNOWN COMPOUNDS PREPARED

Compound	Reference
(R)-1,2-dimethylaminopropane	2,3
$\text{NH}_4[\text{Co(III)}(\text{NH}_3)_2(\text{lpn})(\text{SO}_3)_2]$	12,13
$[\text{Co(III)}(\text{N,N}'\text{-Meen})_2(\text{NO}_2)_2]^+$	2,19
$[\text{Co(III)}(\text{N,N}'\text{-Meen})_2\text{Cl}_2]\text{ClO}_4$	2,19
<u>trans</u> - $[\text{Co(III)}(\text{lpn})_2\text{Cl}_2]\text{Cl}$	35
<u>trans</u> - $[\text{Co(III)}(\text{pn})_2\text{Cl}_2]\text{Cl}$	36
<u>trans</u> - $[\text{Co(III)}(\text{lpn})_2\text{Br}_2]\text{Br}$	37
<u>trans</u> - $[\text{Co(III)}(\text{pn})_2\text{Br}_2]\text{Br}$	36

# ATTEMPTED BUT UNSUCCESSFUL PREPARATIONS

Compound	Method(s)
<u>trans</u> -[Co(III)(N,N'-Meen) <sub>2</sub> Br <sub>2</sub> ]Br	2,19,37
<u>trans</u> -[Co(III)(N,N'-Melpn) <sub>2</sub> Cl <sub>2</sub> ]Cl	35,36
<u>trans</u> -[Co(III)(N,N'-Melpn) <sub>2</sub> Br <sub>2</sub> ]Br	36,37
<u>trans</u> -[Co(III)(N,N'-Eten) <sub>2</sub> Cl <sub>2</sub> ]Cl	2,19,34,35,36
<u>trans</u> -[Co(III)(N,N'-Eten) <sub>2</sub> Br <sub>2</sub> ]Br	2,19,36,37
<u>trans</u> -[Co(III)(NH <sub>3</sub> ) <sub>2</sub> (N,N'-Meen)Br <sub>2</sub> ]Br	12
<u>trans</u> -[Co(III)(NH <sub>3</sub> ) <sub>2</sub> (N,N'-Melpn)Br <sub>2</sub> ]Br	12
<u>trans</u> -[Co(III)(NH <sub>3</sub> ) <sub>2</sub> (N,N'-Eten)Br <sub>2</sub> ]Br	12
<u>trans</u> -[Co(III)(NH <sub>3</sub> ) <sub>2</sub> (N,N'-Et1pn)Br <sub>2</sub> ]Br	12
<u>trans</u> -[Co(III)(NH <sub>3</sub> ) <sub>2</sub> (N,N'-Bz1pn)Br <sub>2</sub> ]Br	12
<u>trans</u> -[Co(III)(NH <sub>3</sub> ) <sub>2</sub> (N,N'-Eten)Cl <sub>2</sub> ]Cl	12,13,31
(-) <sub>D</sub> - <u>trans</u> -[Co(III)(NH <sub>3</sub> ) <sub>2</sub> (N,N'-Eten) <sub>2</sub> -(NO <sub>2</sub> ) <sub>2</sub> ] <sup>+</sup>	2,8,19

## CHAPTER I

### INTRODUCTION

The stereoisomerism of trans-diacido cobalt(III) complexes with (R)-1,2-diaminopropane (lpn) and some of its derivatives has been studied by numerous workers.

(1) The lpn derivative (R)-1,2-dimethylaminopropane (N,N'-Melpn) has been prepared. (2) The stereoisomerism of trans-diacidobis(1,2-diamine)cobalt(III) complexes with N,N'-Melpn and certain other 1,2-diamine ligands has been studied. (2,3) (R)-1,2-Diaminopropane and its derivatives are particularly adapted for the study of the stereoisomerism of trans-diacidobis(1,2-diamine)-cobalt(III) complexes because of the stereospecificity that these enantiomeric 1,2-diamine ligands have when coordinated in the trans-diacidobis(1,2-diamine)cobalt-(III) complexes.

The asymmetric carbon atom in lpn has been shown to exist in the (R)-configuration by Reihlen, Weinbrenner & Hessling, (4) who prepared the levorotary 1,2-diaminopropane enantiomer through conversion of the carboxylic acid moiety in D-alanine into an amino-methyl in the lpn. This (R)-assignment was confirmed when the crystal structure of a single crystal of trans-dichlorobis(lpn)cobalt(III) chloride hydrochloride di-

hydrate was studied by anomalous dispersion x-ray diffraction by Saito & Iwasaki. (5)

Any conversion of the amine groups in lpn by substitution for the amine hydrogens without breaking bonds to the chiral (R) carbon prepares an N-substituted lpn derivative also having the (R)-configuration. In this manner, Tiethof (2) showed that the levorotary 1,2-dimethylaminopropane prepared from lpn by conversion of the amine hydrogens to methylamine groups had the (R)-configuration.

The asymmetric carbon of (R)-1,2-diacetamidopropane prepared from lpn and acetic acid will thus also have an (R)-configuration because the bonds to the chiral carbon remain intact. The asymmetric carbon of the N,N'-diethyl derivative of lpn prepared from reduction of (R)-1,2-diacetamidopropane will likewise have the (R)-configuration. This N,N'-diethyl derivative of lpn is (R)-1,2-diethylaminopropane (N,N'-Et<sub>2</sub>lpn).

The 5-membered chelate rings formed by 1,2-diaminoethane (en) and its C- and N-substituted variants are non-planar due to conformational energy requirements of the ring. Theilacker (6) proposed that en chelate rings take a skew conformation. Corey & Bailar (7) concluded after detailed analysis that chelate rings such as en and pn exist in enantiomeric  $\delta$  or  $\lambda$  skew conformations as shown in Figure 1.

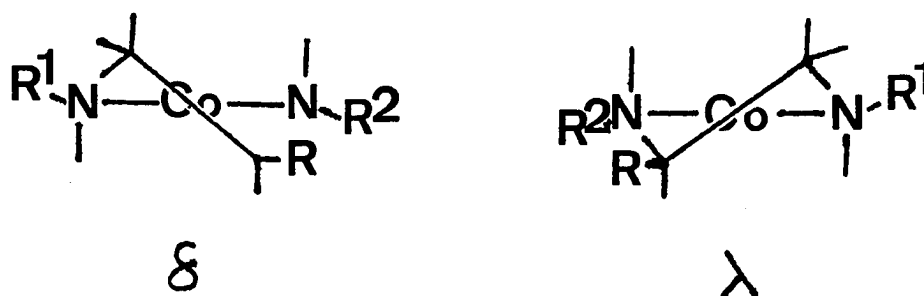


Figure 1. Skew Conformations of Chelated 1,2-Diamine Rings. The  $\delta$ -conformation is on the left, and the  $\lambda$ -conformation is on the right. If R is methyl, and  $R^1$  &  $R^2$  are H, the 1,2-diamine is 1,2-diaminopropane.

Hawkins, (1) and Buckingham, Marzilli & Sargeson (8) after detailed conformational analyses generally concluded that skew conformations such as these allow any C- and N-methyl groups to lie in equatorial positions. In this manner, the chelate ring has more stability and is of a lower energy than if the methyl substituents were in axial positions. This has been borne out by x-ray studies. (5,9) Similarly, generally equatorial orientations can be expected for the N-ethyl groups in chelate rings with N,N'-Et1pn. (10)

Yano, Ito, Koike, Fujita & Saito (11) have shown by proton magnetic resonance (PMR) spectra that in aqueous solutions (R)-1,2-diaminopropane chelate rings orient stereospecifically and have the  $\lambda$ -conformation. Saburi, Tsujito & Yoshikawa (12) have shown that (S)-

1-methylamino-2-amino, (S)-1-amino-2-methylamino and (S)-1,2-dimethylaminopropane (N-Medpn, N'-Medpn and N,N'-Medpn) chelate rings also coordinate stereospecifically onto cobalt(III), but in the opposite  $\delta$ -conformation. Tiethof (2) showed, and Tiethof & Cooke (3) reported that (R)-1,2-dimethylaminopropane chelate rings coordinate stereospecifically in the  $\lambda$ -configuration in trans-diacidobis((R)-1,2-dimethylaminopropane)cobalt(III) complexes. (R)-1,2-Diethylaminopropane also should coordinate stereospecifically in stable trans-diacidobis((R)-1,2-diethylaminopropane)cobalt(III) complexes in the  $\lambda$ -configuration. (10) This is because of the (R)-configuration (which N,N'Et1pn has) about the asymmetric carbon and the equatorially orienting C-methyl and N- and N'-ethyl groups.

The circular dichroism (CD) spectra of trans-diacidobis(N<sub>4</sub>)cobalt(III) complexes having one to two 5-membered diamine chelate rings is characteristic of the geometry of the complexes. (1) Various regional rules have been put forth to relate the observed CD spectra and the stereochemistry of complexes which are optically active such as these. (13,14,15,16) The underlying geometry of these complexes is illustrated in Figure 2.

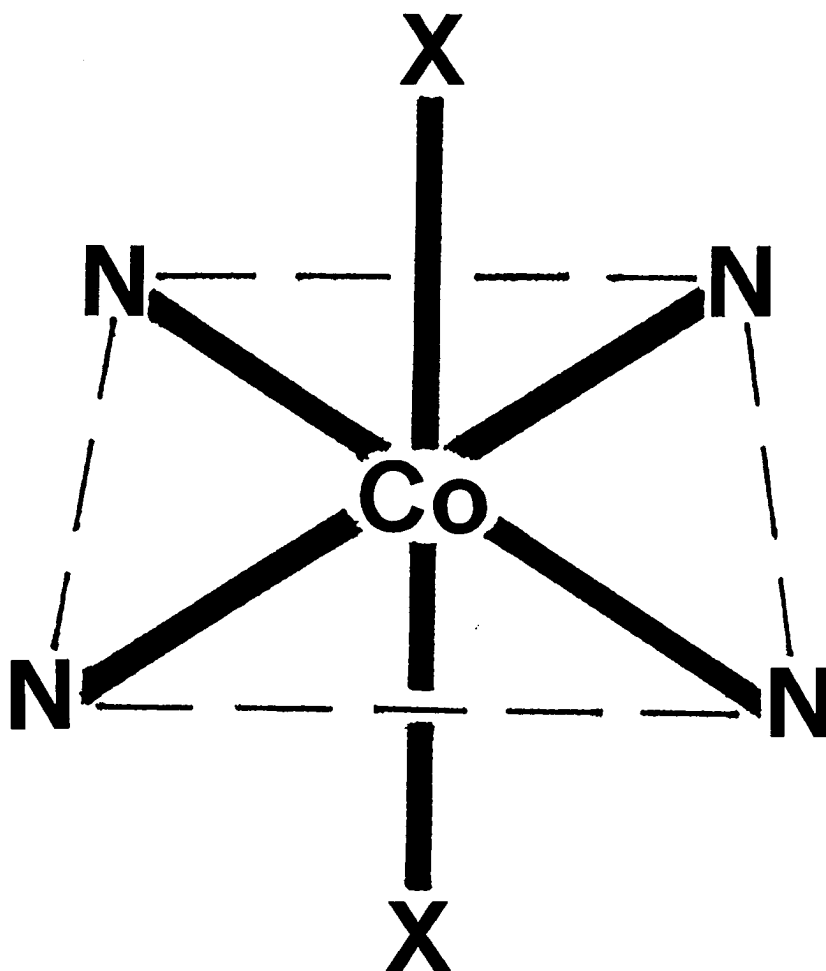


Figure 2. Underlying Geometry of trans-[Co(III)N<sub>4</sub>X<sub>2</sub>]<sup>+</sup> Complexes. Each X represents a coordinated acido group. Each N represents a coordinated nitrogen such as from ammonia or a 1,2-diamine ligand. Solid lines represent bonds to the cobalt(III). Dotted lines between any two N atoms indicate lines on the Co(III)N<sub>4</sub> plane. The dotted lines do not represent N-N bonds.

One such rule is the hexadecadal sector rule of Mason. (14) In this rule, the sign of the Cotton effect observed in the CD spectra which is induced in the trans-[Co(III)N<sub>4</sub>X<sub>2</sub>]<sup>+</sup> chromophore is related to the presence of substituents in sixteen sectors defined by the Co(III)N<sub>4</sub> plane. These sectors are illustrated in Figure 3.

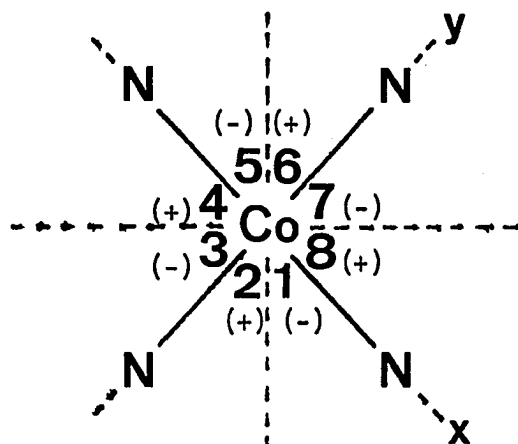


Figure 3. Hexadecadal Rule Sectors. The +z direction is up from the plane of the page, toward the reader. Sectors in the +z direction are indicated as +1 sector, etc. The -z direction is down from the plane of the page, and sectors in the -z direction are indicated as -1 sector, etc. The signs for the A<sub>1g</sub> → A<sub>2g</sub> (D<sub>4h</sub>) d-d transition observed in the CD spectra which are induced by substituents in the +z sectors are shown in parenthesis.

For the trans-[Co(III)N<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup> chromophore A<sub>1g</sub> → A<sub>2g</sub>(D<sub>4h</sub>) d-d transition near 21,500 cm<sup>-1</sup>, substituents in each of the odd numbered sectors induce negative CD spectra effects in the +z direction, whereas substituents in each of the even numbered sectors induce posi-



tive CD spectra effects in the +z direction. The effects are all opposite in the -z direction. The qualitative effects are opposite to the  $A_{1g} \rightarrow A_{2g}(D_{4h})$  transition effects for the  $A_{1g} \rightarrow E_g(D_{4h})$  component of the  $A_{1g} \rightarrow T_{1g}(O_h)$  cobalt(III) d-d transition, which lies near to  $16,000 \text{ cm}^{-1}$  for the trans- $[\text{Co(III)}\text{N}_4\text{Cl}_2]^+$  chromophore. Thus, for example, if a substituent is in the -2 sector, like the methylene of the  $\lambda$ -chelated lpn is, a negative  $A_{1g} \rightarrow A_{2g}(D_{4h})$  transition CD spectra effect and a positive  $A_{1g} \rightarrow E_g(D_{4h})$  transition CD spectra effect is induced by its presence there.

Mason (14) applied his rule only to X groups in approximately tetragonal trans- $[\text{Co(III)}\text{N}_4\text{X}_2]^+$  chromophores which had cylindrical ( $C_\infty$ ) symmetry, such as chloride, about the X-Co-X axis. Where X was  $\text{NO}_2^-$  in the chromophore, the position of the oxygen atoms of the nitro groups was not specifically known, and it was noted that ignoring this (i.e., assuming the nitro groups were cylindrically symmetrical) the sign of the CD spectra of the trans,trans-dinitrobis(1-methylamino-2-aminoethane)cobalt(III) chromophore in the  $A_{1g} \rightarrow T_{1g}(O_h)$  region was opposite to that of the  $A_{1g} \rightarrow A_{2g}(D_{4h})$  transition observed in the CD spectra of the corresponding trans-dichloro chromophore. (14) This has been noted by many other workers. (2,12,15,17) Bosnich & Harrowfield (15) noted it not only for the trans-di-

nitro( $N_4$ )cobalt(III) chromophore but also for the corresponding trans-chloronitro chromophore. Apparently, the hexadecadal rule was useful only for a limited class of trans- $[Co(III)N_4X_2]^+$  chromophores with discernable tetragonal field transitions.

However, the hexadecadal rule has a theoretical basis as well. Shellman (18) showed on symmetry considerations alone that perturbing functions have symmetry properties of a pseudoscalar in the point group of the unperturbed chromophore. The simplest form for this function in the  $D_{4h}$  point group is  $XYZ(x^2-y^2)$  which results in the sixteen sectors when its regional sign dependancy is considered. The trans- $[Co(III)N_4X_2]^+$  chromophore is approximately of  $D_{4h}$  symmetry. By this reasoning, not only should the hexadecadal rule apply to cases where the trans-acido groups are cylindrically symmetrical but also for the cases involving nitro groups.

Optically active complexes with 5-membered 1,2-diaminoalkane chelate rings with 1,2-diethylamino groups are generally absent from the field of the trans- $[Co(III)N_4X_2]^+$  chromophores studied in relation to the hexadecadal rule. Even though at first glance such proposed complexes appear to be mere structural analogs of the corresponding complexes with 5-membered chelate rings with 1,2-dimethylamino groups, their actual synthesis may not be so straightforward.

There has been no report of the preparation and resolution of trans-[Co(III)(N,N'-Eten)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]Cl. Tiethof & Cooke (19) reported the resolution of the corresponding N,N'-Meen complex with (+)silver- $\alpha$ -bromocomphor- $\pi$ -sulfonate. There has been no report of the preparation of a trans-diacidobis(N,N'-Etlpn)cobalt(III) complex and its optical study.

The preparation of trans-[Co(III)(NH<sub>3</sub>)<sub>2</sub>(lpn)Br<sub>2</sub>]Br has been reported. (13) Analogous bromides with the 1,2-diamines of N-Medpn and N'-Medpn have been reported. (12) The analogous complex with N,N'-Medpn has not been reported.

The preparation of trans-[Co(III)(NH<sub>3</sub>)<sub>2</sub>(lpn)Cl<sub>2</sub>]-HSO<sub>4</sub> and the corresponding perchlorate salt has been reported. They were each prepared through the trans-[Co(III)(NH<sub>3</sub>)<sub>2</sub>(lpn)Br<sub>2</sub>]<sup>+</sup> complex. (13,15) Saburi, Tsujito & Yoshikawa (12) reported that the trans-[Co(III)(NH<sub>3</sub>)<sub>2</sub>(1,2-diamine)Br<sub>2</sub>]Br complexes with 1,2-diamines of N-Medpn and N'-Medpn which they prepared were prepared in view of the fact that the corresponding trans-dichloro complexes readily formed cis-dichloro complexes.

The preparation of trans-[Co(III)(N,N'-Melpn)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> complexes has been reported by reaction of corresponding dinitro complexes with hot HCl. (2,3) This method was reported to be successful in converting the corres-

ponding dinitro complexes into trans-[Co(III)(N-Medpn)<sub>2</sub>-Cl<sub>2</sub>]<sup>+</sup> and trans-[Co(III)(N'-Medpn)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> complexes but not successful in converting the trans-[Co(III)(N,N'-Medpn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> complex. (12) The HCl conversion of trans-[Co(III)(N-Meen)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]ClO<sub>4</sub> into trans-[Co(III)-(N-Meen)<sub>2</sub>NO<sub>2</sub>Cl]ClO<sub>4</sub> has been reported. (17) Analogous conversions with HBr have not been reported.

In addition, trans-[Co(III)N<sub>4</sub>I<sub>2</sub>]<sup>+</sup> complexes are lacking. Cobalt(II) iodides are known. Iodide ions are oxidized to iodine, preventing formation of the trans-[Co(III)N<sub>4</sub>I<sub>2</sub>]<sup>+</sup> complexes. (20)

Apparently, there is some practical limit to the trans-[Co(III)N<sub>4</sub>X<sub>2</sub>]<sup>+</sup> complexes which may be prepared and isolated for study. There appears to be some order to the relative instability brought on by substituting more freely conforming 1,2-dimethylamino and 1,2-diethylamino groups onto 1,2-diamine chelate rings, the type and number of chelate rings on the complex and the type of acido substituent. There also appears to be some relative order of successful methods to be employed in preparing the marginally stable complexes. The counterion of the complexes may play a part in the stability considerations.

## CHAPTER II

### PROPOSAL

#### Objectives

The objectives of this study were to improve the preparation of lpn and to prepare the new 1,2-diamines, N,N'-Etlpn and N,N'-Bzlpn. They were also to investigate preparation of optically active trans-[Co(III)N<sub>4</sub>X<sub>2</sub>]<sup>+</sup> complexes with Cl<sup>-</sup>, Br<sup>-</sup> and NO<sub>2</sub><sup>-</sup> acido groups and NH<sub>3</sub> and 1,2-diamine N-ligands and to determine the practical limits of preparing new optically active trans-[Co(III)N<sub>4</sub>X<sub>2</sub>]<sup>+</sup> complexes, especially bis(1,2-diamine) complexes with N,N'-Eten and N,N'-Etlpn. In addition, the synthetic investigation was to include trans-[Co(III)(NH<sub>3</sub>)<sub>2</sub>(1,2-diamine)X<sub>2</sub>]X complexes with X of Br<sup>-</sup> or Cl<sup>-</sup> and 1,2-diamines, N,N'-Meen; N,N'-Melpn; N,N'-Eten; N,N'-Etlpn; and N,N'-Bzlpn. Those new trans-[Co(III)-N<sub>4</sub>X<sub>2</sub>]<sup>+</sup> complexes which could be synthesized were to have their CD spectra and stereochemistry analyzed along with an analogous structural series of known complexes and the hexadecadal rule. A particular object of this study was to analyze trans-[Co(III)(1,2-diamine)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> complexes in terms of the hexadecadal rule, including the new trans-[Co(III)(N,N'-Etlpn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> complex.

## Achievements

The achievements of this study included improved 1pn production and preparation of the new 1,2-diamines, N,N'-Etlpn and N,N'-Bzlpn. The achievements also included preparation of the new optically active complex trans-[Co(III)(N,N'-Etlpn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]Cl and resolution into its trans,trans- and trans,cis- isomers. Also achieved were the preparation of new intermediate complexes NH<sub>4</sub>-[Co(III)(NH<sub>3</sub>)<sub>2</sub>(1,2-diamine)(SO<sub>3</sub>)<sub>2</sub>] with the 1,2-diamines of N,N'-Meen; N,N'-Melpn; N,N'-Eten; N,N'-Etlpn; and N,N'-Bzlpn, the preparation of the new trans-[Co(III)-(NH<sub>3</sub>)<sub>2</sub>(1pn)Cl<sub>2</sub>]Cl and the determination of some practical limits of preparing many complexes. The relationship between the CD spectra and stereochemistry of the trans-[Co(III)(1,2-diamine)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> complexes, including the new trans-[Co(III)(N,N'-Etlpn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> isomers, was analyzed with the hexadecadal rule. The position of the nitro groups in these trans-dinitro complexes has been determined for the first time.

## CHAPTER III

### EXPERIMENTAL

#### Materials

Chemicals were used as commercially obtained unless otherwise noted. The 1,2-dialkylaminoethanes were redistilled.

#### Characterizations

Melting points were taken on a Hoover capillary melting point apparatus.

The IR spectra were taken on a Perkin-Elmer Model 457 or Beckman Acculab 8 recording spectrophotometer. Solid samples were done in potassium bromide discs. Miss Christine Ann Jensen did many of these. The IR spectral data is reported in reciprocal centimeters.

The UV-visible spectra were taken on a Beckman Series 30 UV-Visible recording spectrophotometer by Mrs. Donna Fielding of The Dow Chemical Company in Midland, Michigan.

Circular birefringence data were taken on a Beckman Model DU-2 spectrophotometer with a Keston Model D polarimeter attachment. The sample cell was 5.00 cm.

The CD spectra were taken at 30°C on a Jasco Model

J-20 recording spectrophotometer standardized with 0.062% aqueous D-10-camphorsulfonic acid solution at the Michigan Molecular Institute in Midland, Michigan. The sample cell was 1.000 cm. Assistance was provided by Mr. Steve Keinath.

The PMR spectra were taken on a Bruker Model WM-360WB 360 MHz recording spectrometer with an internal standard of sodium trimethylsilylpropanesulfonate by Mr. Gary L. Jewett of The Dow Chemical Company in Midland, Michigan. Samples of dichloro complexes were taken in 0.2 N DCl/99% D<sub>2</sub>O; dinitro in 99% D<sub>2</sub>O.

Titration of free amines were done potentiometrically in carbonate-free aqueous solutions with a Beckman Model SS-2 pH meter. The titrant was aqueous hydrochloric acid, standardized with sodium carbonate. The HCl concentrations ranged from 0.302 to 0.314 N.

Most C,H,N elemental analyses were done by Midwest Microlab, Ltd., Indianapolis, Indiana. Compounds which were analyzed for Co, C, H, N (and Na) were done by Messrs. Ward L. Rigot and Steve Konopnicki of The Dow Chemical Company in Midland, Michigan.

#### Preparation of Diamines

##### (R)-1,2-Diaminopropane

Racemic 1,2-diaminopropane was resolved by the



method of Dwyer, Garvan & Shulman. (21) Resolution was stopped at the tenth recrystallization. M.p.: 141-144°C.

The resolved diastereomer salt batches were each converted to the dihydrochloride salt by the method of Bailar, Jonassen & Gott. (22) M.p.: 138-144°C, with decomposition.

Batches of the dry dihydrochloride salt were each intimately mixed in a 500-mL glass distilling flask with a volume of potassium hydroxide pellets three times the volume of the dihydrochloride salt. The flask was equipped with a short Vigreux column and a water-cooled condenser. Venting was through a drying tube containing calcium sulfate. The flask contents were subjected to gentle reflux, then simple distillation, heating with a flame. Yields from the dihydrochloride salt were about 90% of theory.

Samples were titrated to determine concentrations and had their density, and optical rotation determined in dry benzene. The following was obtained for 1pn batches (indicated by Roman numerals). Fraction I (distilled from moist 1pn·2HCl): head T, 112-114°C; concentration, 84.6% (aq); density, 0.89 g/mL at 0°C, 0.88 g/mL at 5°C, 0.88 g/mL at 10°C, 0.875 g/mL at 20°C;  $[\alpha]_D^{25}$ , -34.3°. Fraction IIa: head T, 114-117°C; concentration, 95.1% (aq); density, 0.875 g/mL at 20°C;

$[\alpha]_D^{20}$ , -34.2°. Fraction IIb: head T, 117-119°C; concentration, 95.2% (aq); density, 0.873 g/mL at 20°C;  $[\alpha]_D^{20}$ , -34.2°. The aqueous concentration of other lpn fractions obtained from mixing KOH with a concentrated lpn·2HCl(aq) solution or mixing solid lpn·2HCl with solid NaOH were 35-75% or were 60%, respectively.

The 85-95% lpn fumed on exposure to moist air. It was stored for years without visible change in glass bottles with greased ground glass stoppers.

A dibenzoyl derivative was prepared. (23) M.p.: 192.5-194.5°C.

#### (R)-1,2-Diethylaminopropane

The new 1,2-diamine, (R)-1,2-diethylaminopropane, was prepared by lithium aluminum hydride reduction of (R)-1,2-diacetamidopropane (the (R)-bisamide). The (R)-bisamide preparation from lpn was analogous to the method of Adams, Johnson & Wilcox. (24) The reduction step was analogous to the method of Rice, Armbrecht, Grogan & Reid. (25)

#### (R)-1,2-Diacetamidopropane

In preparing the (R)-bisamide, 16.75 g of 84.6% lpn with  $[\alpha]_D^{25}$  of -34.3° and a few boiling chips were put into a round bottom flask equipped with a

Vigreux column. Then 24.1 mL of glacial acetic acid was added dropwise. A water-cooled condenser was attached on the column, and the flask contents were heated with a flame, collecting no distillate for one half hour. The intensity of heating was increased so that 9 mL of slightly acidic distillate was slowly and steadily collected at a head temperature of about 99-100°C over a period of one hour. The yellow flask contents were further heated so that 0.3 mL of acidic distillate was collected at 100-125°C. After cooling in air for five minutes, the contents of the flask were poured into one liter of benzene, with stirring. Crystals formed. A second crop was obtained with cooling. Each crop was suction filtered and washed with anhydrous diethyl ether (anhydrous ether). Purification was done by slurrying in boiling benzene, cooling, suction filtering and washing with anhydrous ether. The step beginning with slurrying was then repeated using boiling ether instead of benzene. Contaminating liquid layers were separated. The impure crystals were very hygroscopic. This alternating slurrying process ending with the ether slurry was repeated until a sharp melting point was obtained. The (R)-bisamide was dried in vacuo.

The purified first crop was the most pure: m.p., 153.5-154.0°C after purification as above. Elemental

analysis, calculated for  $C_7H_{14}N_2O_2$ : C, 53.31%; H, 8.92%. Found: C, 52.74%; H, 9.10%.

The IR spectra of the (R)- and racemic bisamide prepared by the same process were equivalent. The IR spectra is reproduced in Figure 4.

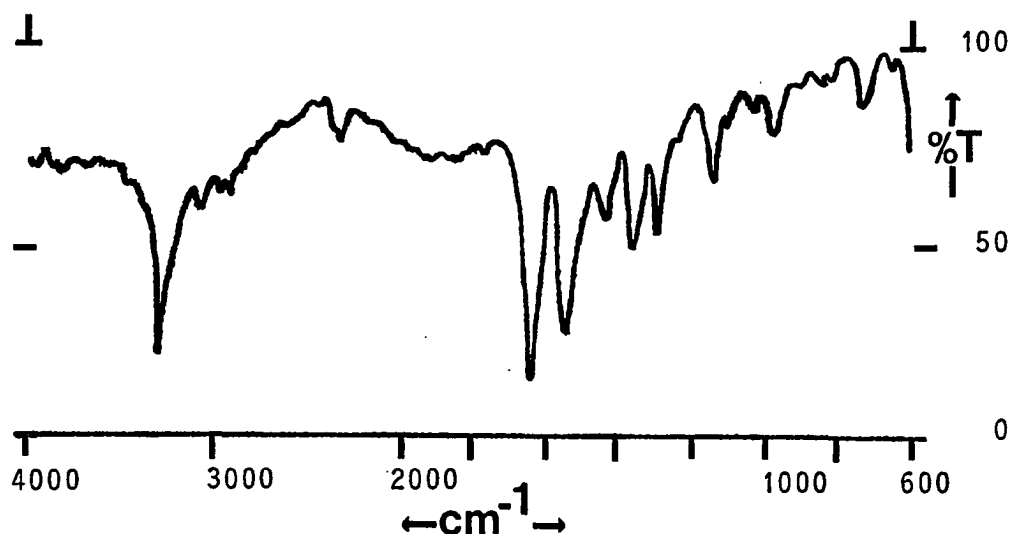


Figure 4. The IR Spectra of 1,2-Diacetamidopropane in a KBr Disc.

(R)-Batches gave very fine, white needles which melted from 152.5°C to 154.8°C. The total yield of (R)-1,2-diacetamidopropane from the foregoing method was 15.21 g (50.3% of theory).

A yield of greater than 60% of the (R)-bisamide was obtained when 0.5 mole of 95% lpn with  $[\alpha]_D^{20}$  of  $-34.2^\circ$  was used as the starting material, and the hot

crude (R)-bisamide was heated over the course of about two and one half hours. No distillate was collected over the first hour; 23 mL was collected at a head temperature of 99-100°C over the next hour and a half. The final six minutes of heating resulted in 1 mL of distillate collected at 105-120°C (3 minutes) and 1 mL finally at 120-180°C. The hot crude (R)-bisamide was poured into one liter of boiling benzene, with stirring, purifying the batch by the foregoing alternating slurrying process. M.p.: 153°C-154.5°C.

(R)-1,2-Diethylaminopropane from the (R)-Bisamide

In the reduction step, 14.15 g of the (R)-bisamide (m.p., 152.5-154.8°C) was slurried in 800 mL of anhydrous ether, and this slurry added over ten minutes to a stirred slurry of 12 g of lithium aluminum hydride and 200 mL of anhydrous ether in a 2-liter 3-neck flask equipped for reflux. With continual stirring, the contents of the flask were gently refluxed for six hours, then cooled in an ice bath and slowly quenched with the dropwise addition of 23 mL of water, which formed a white solid.

This solid was suction filtered from the ethereal solution containing N,N'-Et1pn and washed with ether, saving the ethereal washings and the filtrate. The solid was slurried in ether, and 3 mL of water and

5-10 g of sodium hydroxide pellets were added. The alkalized solid was suction filtered and washed with ether, saving the ethereal solutions. The solid was re-slurried, wetted and alkalized, filtered and washed two additional times in this manner, again saving the ethereal solutions. All ethereal portions were combined, dried over 10-20 sodium hydroxide pellets and evaporated under vacuum to about 30 mL and filtered of unreacted (R)-bisamide. This concentrated solution was distilled over a few potassium hydroxide pellets from a 50-mL round bottom glass flask equipped with a Vigreux column, heating with a flame. Venting was through a drying tube containing calcium sulfate.

The yield of colorless N,N'-Et1pn collected at a head temperature of 153-156°C at 745 mm Hg was 7.34 g (54.4% of theory based on the (R)-bisamide). It had a concentration of 86.3% by weight and  $K_{b1}$  of  $9 \times 10^{-5}$  and  $K_{b2}$  of  $2 \times 10^{-10}$  as determined from HCl titration curves. The  $[\alpha]_D^{20}$  in dry benzene (0.01 g/10 mL) was  $-59^\circ$ . Reduction of larger batches of (R)-bisamide by this method resulted in no improvement in yield. Combining smaller batches of ethereal solutions of N,N'-Et1pn such as in the foregoing batches for distillation gave yields which were 60% of theory based on the (R)-bisamide.

Free N,N'-Et1pn formed a mist above the liquid

surface upon exposure to moist air and had a sharp but clammy ammonia-like odor. It seemed to have an anorectic effect on human physiology from incidental vapor and skin contact. It was stored in glass bottles with greased ground glass stoppers.

A sample was converted to the dihydrochloride salt by the addition of concentrated hydrochloric acid to its ethanolic solution. It was triturated under anhydrous ether and dried in vacuo. Elemental analysis, calculated for  $C_7H_{20}N_2Cl_2$ : C, 41.39%; H, 9.92%. Found: C, 40.64%; H, 9.67%. M.p.: 210-220°C, with decomposition. The IR spectra is reproduced in Figure 5.

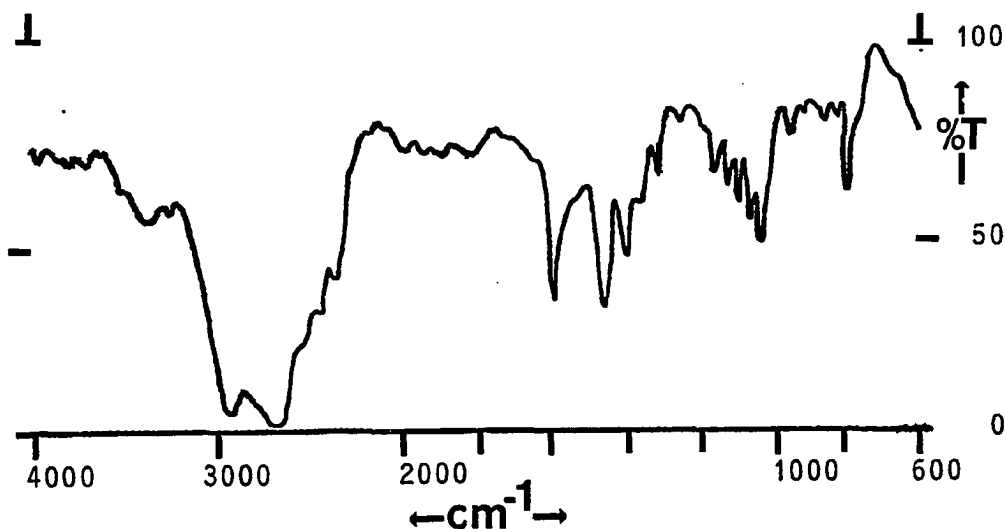


Figure 5. The IR Spectra of  $N,N'$ -Etpn·2HCl in a KBr disc.

(R)-1,2-Dibenzylaminopropane

The new 1,2-diamine, (R)-1,2-dibenzylaminopropane, was prepared by reduction of the Schiff's base from the reaction of benzaldehyde with lpn. The reduction was carried out with slurried ethereal lithium aluminum hydride or methanolic sodium borohydride. (27,28,29)

The Schiff's base was prepared by combining 4.2 g of 95% aqueous (R)-1,2-diaminopropane and then 12.5 g of 99% benzaldehyde in a 250-mL Erlenmeyer flask. After heat evolution ceased, 100 mL of ether was added and mixed. An aqueous layer was separated from the ethereal layer, and the ethereal layer was saved. Then 70 mL of benzene was added, and the mixture was heated over a steam bath to evaporate the ether, the benzene-water azeotrope and the remaining benzene.

Next, 100 mL of anhydrous ether was added, and the mixture was placed in a 500-mL 3-neck flask equipped for reflux. An ether slurry with 8 g of  $\text{LiAlH}_4$  was added slowly with stirring, and the flask contents were refluxed for 1 hour. Then 30 mL of water was added dropwise with stirring in an ice bath to quench the reaction and the product was worked up as was the N,N'-Et1pn.

Alternatively, methanolic sodium borohydride was used to reduce the Schiff's base. Methanol was used in



place of the ether. The reaction was quenched by merely heating the methanolic sodium borohydride.

The product was yellow and oily, and it had a fishy odor which was characteristically amine-like. It was difficult to purify by distillation (head T: 220-260°C), gas chromatography (gumming of the column) or precipitation of the HCl salt (even dry HCl caused a gummy solid with pink by-product in diethyl ether). It was levorotary at the sodium D-line (589 nm) and at the mercury green line (546 nm). It seemed to have an anorectic effect on the human physiology which was more pronounced than the anorectic effect of N,N'-Et1pn.

The dibenzoyl derivative of 1pn could not be reduced to N,N'-Bz1pn by lithium aluminum hydride. The attempted reaction was carried out in an ether slurry for 10 hours at reflux.

#### 1,2-Dimethylaminopropane

1,2-Dimethylaminopropane was prepared through the new method which involved the addition of methyl iodide to the Schiff's base formed from reaction of pn and benzaldehyde in a pn to benzaldehyde molar ratio of 1:2. The method was analogous to the method of Morrison & Rinderknecht. (26) A 400-mL soft drink bottle was used as the bomb vessel.

The Schiff's base was prepared by combining 4.2 g

of 95% 1,2-diaminopropane (0.06 mole) and then 12.5 g of 99% benzaldehyde (0.12 mole) in a 250-mL Erlenmeyer flask. After heat evolution ceased, 100 mL of ether was added and mixed. An aqueous layer was separated from the ethereal layer, saving the ethereal layer. Then 70 mL of benzene was added, and the mixture was heated over a steam bath to evaporate the ether, the benzene-water azeotrope and the remaining benzene.

Next, 20.3 g of methyl iodide (0.14 mole) was added, and the mixture was placed in the bomb and stoppered. The bomb contents were heated at 80°C for 12 hours. The oil produced was mixed with 25 mL of water, followed by 10 g of KOH. Distillation followed.

The yield of 1,2-dimethylaminopropane was 10% of theory based on pn. Elemental analysis showed the ratio of C/N within 5% of theory.

#### (R)-1,2-Dimethylaminopropane

(R)-1,2-Dimethylaminopropane was prepared by the lithium aluminum hydride reduction of (R)-diethylpropylenebiscarbamate (the (R)-biscarbamate) (m.p. 94.5-96.0°C). (2) The (R)-biscarbamate was prepared from 85% lpn with  $[\alpha]_D^{25}$  of -34.3° by the method of Tiethof. (2) Yields of N,N'-Melpn were about 30% of theory based on the (R)-biscarbamate.

A fraction of 74.7% concentration as determined by

HCl titration was collected at a head temperature of 124-129°C. The  $[\alpha]_D^{25}$  in dry benzene was  $-53.6^\circ$  at 0.15 g/10 mL. The maximum concentration of the N,N'-Melpn fractions obtained was 82%.

### Preparation of Complexes

#### $[\text{Co(III)(N,N'-Et1pn)}_2(\text{NO}_2)_2]^+$ Complexes

##### Chloride Counterion Complex

The complex was prepared by the a method analogous to the method of Tiethof & Cooke. (19) Hydrogen peroxide was used as the oxidant. (30)

An ice-cold solution of 1.00 g of 95% N,N'-Et1pn (0.00768 mole) in 10 mL of water containing 0.38 g of 37% HCl(aq) (0.0039 mole) was added with stirring to an ice-cold solution of 0.91 g of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.0038 mole) in 10 mL of water, and 0.53 g of  $\text{NaNO}_2$  was added quickly. The mixture was stirred in an ice bath for 5 minutes, and it turned yellow-green. Next, 2 mL of ice-cold 30%  $\text{H}_2\text{O}_2$ (aq) was added dropwise with stirring, adding 2 mL of ether as needed to control foaming. (29) A brown solution formed. The solution was stirred in the ice bath for 15 minutes, was removed from the ice bath and stirred another 15 minutes and was then heated on a steam bath for 15 minutes. Fine precipitation

occurred, and the mixture was evaporated to dryness at room temperature under an air stream. The solid was triturated under 50 mL of methanol and filtered. The filtrate was evaporated to dryness at room temperature under an air stream and then dried in a 70°C oven for 2 hours. The solid was ground with a mortar and pestle to give a dull orange product. The yield before chromatography was 1.6 g. The complex slowly, visibly decomposed as a solid. The IR spectra of the product had strong absorptions at  $1410\text{ cm}^{-1}$  and  $1310\text{ cm}^{-1}$ , which is indicative of the presence of some cis-dinitro isomers, as discussed in the Results and Discussion section.

#### Perchlorate Counterion Complex

The complex was prepared as above and precipitated as the perchlorate salt before chromatography. (19) The yield of the perchlorate salt complex before chromatography was 1.0 g from 1.43 g of the  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ . No decomposition (visible to the naked eye) of the precipitated perchlorate was observed over the course of ten months.

#### Bromide Counterion Complex

The complex was prepared analogously to the method for the chloride counterion complex, but  $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$  was

used as a reactant. The yield of the bromide salt complex before chromatography was 2.4 g from 1.25 g of the  $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$ . No decomposition (visible to the naked eye) was observed over the course of eight months.

#### Nitrate Counterion Complex

The nitrate salt complex was prepared by a method analogous to the method of Bailar, Holtzclaw, Sheetz & McCarty. (31) Air oxidation was for 10 hours. The orange/brown product was difficult to precipitate, but it precipitated on cooling from ethanol after preliminary filtration of a light colored solid from an aqueous mixture. Yield: 0.01 g.

The IR spectra showed strong absorptions at 1390; 1310; and  $1410\text{ cm}^{-1}$ . The PMR spectra had signals at 1.28; 1.34; 1.36; 1.39; 1.41; 1.47; 1.48; 2.2-2.4; 2.8; 3.0; and 3.1 ppm. The CD spectra in water (0.059%) and in methanol (0.073%) are reported in the Results and Discussion section.

#### trans-Dinitro Isomers by Chromatographic Resolution

Resolution of the complexes was on a 3.5 cm x 60 cm diameter column. The column was filled to the 50 cm mark with Dowex 50W-X8 100-200 mesh cation exchange resin in the ammonium ion form. (2,3)

The 1.6 g of  $[\text{Co(III)}(\text{N,N'-EtIpn})_2(\text{NO}_2)_2]\text{Cl}$  was

dissolved in 100 mL of water and filtered. The filtrate was added at the rate of 2 mL per minute onto the resin, and water was added at the same rate until the liquid above the resin was no longer colored. The dull orange layer at the top of the resin was then eluted with 40 liters of 0.075 M  $\text{NaClO}_4(\text{aq})$  at a rate of about 1-2 mL per minute. After this elution, the dull orange starting band had been eluted a distance 16-39 cm from the origin and was a more vivid orange. There was also another orange band 2-7 cm from the origin (presumably cis-dinitro complexes (2)) and a dull green-brown band from near the origin to 1 cm from the origin (presumably +2 and +3 cationic complexes and a by-product of  $[\text{Co(III)(N,N-EtIpn)}_2\text{Cl}_2]^+$  complexes (2)). The orange band found 16-39 cm from the origin was assigned as containing the trans-dinitro isomers. (2) The trans-band was removed from the column by a suction hose in the following identified two slowly eluting (s) fractions, one medium-rate eluting (m) fraction and two fast eluting (f) fractions at the indicated distance in centimeters from the origin: Is, 16-21; IIs, 21-26; m, 26-29; If, 29-34; IIf, 34-39.

Each fraction was removed from the resin by 1 N aqueous sodium chloride, and after drying each was taken up into ethanol and redried. Precipitated perchlorate salts could not be obtained, presumably

because the yields after chromatography were too low.

The solid orange trans-dinitro band fractions began to turn to green. The s fractions turned green most readily, noticeably starting within about a week. The m fraction was intermediate in this behavior, and the f fractions took several months to visibly start turning green. The f fractions retained their overall yellow/brown color over the course of ten months.

The IR spectra (IIf) showed a strong absorption at  $1400\text{ cm}^{-1}$ . No absorption near  $1300\text{ cm}^{-1}$  was observed.

The UV-visible spectra (If) in water (0.3%) showed a maximum absorption at 343 nm. The CD spectra (If) in methanol (0.6%) and in water (1.3%) are reported in the Results and Discussion section.

Elemental analysis was conducted on the If fraction of the trans-dinitro band. It showed that the complex was heavily contaminated with sodium salts.

The PMR spectra of the IIf trans-dinitro band fraction initially gave a very broad signal. Filtering with a syringe filter eliminated this, and a sharper spectra was obtained, which is reproduced in Figure 6.

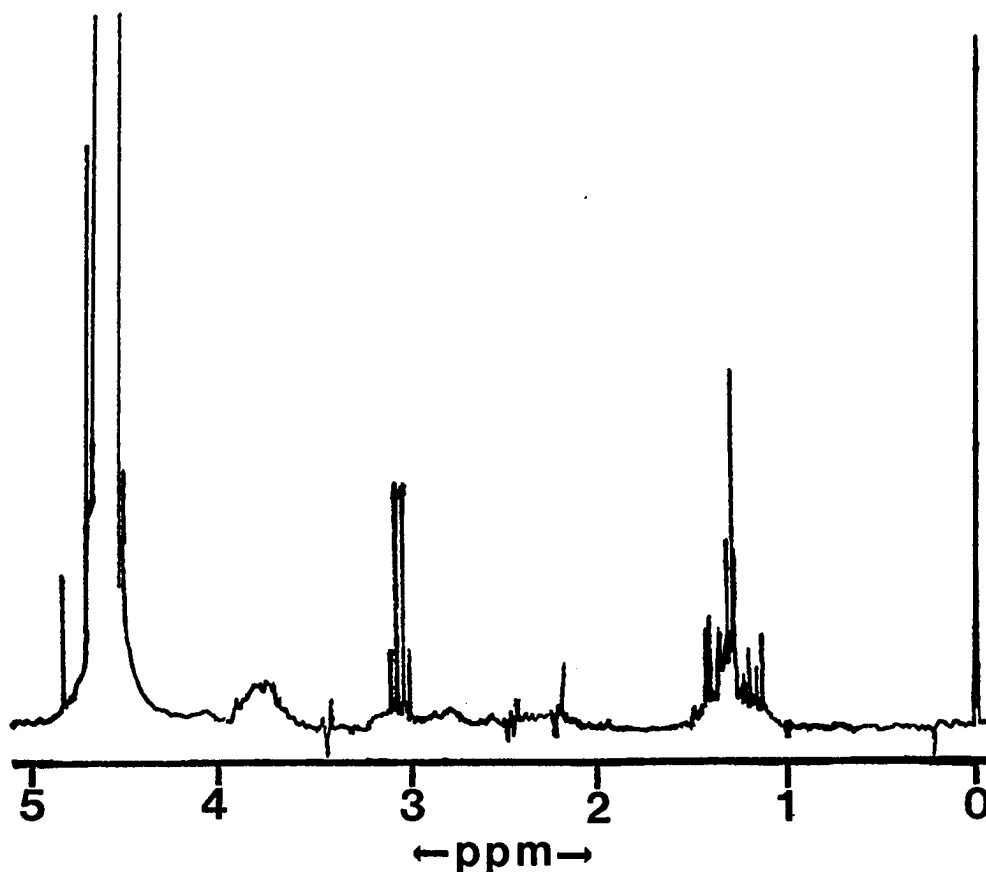


Figure 6. The PMR Spectra of IIf  $[\text{Co(III)(N,N'-Et1pn)}_2(\text{NO}_2)_2]^+$  in  $\text{D}_2\text{O}$ .

The If and IIf trans-dinitro band fractions were combined, dissolved in water, filtered and rechromatographed on Dowex 50W-X8 in the  $\text{NH}_4^+$  form, eluting with 0.1 N  $\text{NaClO}_4(\text{aq})$ . The aqueous f-eluent from the rechromatography of the combined (If + IIf) fractions was evaporated.

The CD spectra of this rechromatographed f-eluent in 20%  $\text{NaClO}_4(\text{aq})$  is reported in the Results and Dis-



cussion section. The PMR spectra of this rechromatographed f-eluent was taken, and it was equivalent to the PMR spectra of the original IIf trans-dinitro band fraction after filtration, but 1800 scans were needed to produce the spectra. The PMR spectra was recorded to include additional peaks at 6.7, 6.9 and 7.1 ppm.

In another resolution,  $[\text{Co(III)(N,N'-Et1pn)}_2(\text{NO}_2)]^+$  chloride, perchlorate and bromide counterion complexes were combined and loaded onto the column with Dowex 50W-X8 in the  $\text{NH}_4^+$  form. The entire trans- band was formed as above but was eluted with 1 N  $\text{NaClO}_4(\text{aq})$  without fractionation. The CD spectra of this eluent is reported in the Results and Discussion section.

#### $\text{trans-[Co(III)(N,N'-Et1pn)}_2\text{Cl}_2]\text{Cl}$

The green/brown band left at the origin from the chromatographic resolution of  $[\text{Co(III)(N,N'-Et1pn)}_2(\text{NO}_2)_2]\text{Cl}$  (made from  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ) was placed over 20 mL of Dowex 50W-X8 in the  $\text{H}^+$  form. This band contained the green trans- $[\text{Co(III)(N,N'-Et1pn)}_2\text{Cl}_2]\text{Cl}$ . (2) Elution was with 0.3 N HCl in methanol, and the bright green band of the trans-dichloro complex was collected. (32) The methanolic eluent was left to evaporate, and the complex decomposed into a cobalt(II) compound, which was indicated by a blue color. (30)

$[\text{Co(III)(N,N'-Alkylen)}_2(\text{NO}_2)_2]\text{ClO}_4$  Complexes

These complexes were prepared with the 1,2-dialkyl-aminoethanes: (a) N,N'-Meen and (b) N,N'-Eten. The N,N'-Meen complex has been reported, (2,19) but the N,N'-Eten complex has not been reported. Preparations were analogous to the method used to prepare the  $[\text{Co(III)(N,N'-Et1pn)}_2(\text{NO}_2)_2]\text{ClO}_4$  as above, but each preparation used 0.1 mole of reactant  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ . Yields: (a), 32%; (b), 14%. The preparation of the complex with N,N'-Eten follows.

$[\text{Co(III)(N,N'-Eten)}_2(\text{NO}_2)_2]\text{ClO}_4$

To an ice-cold solution of 23.8 g of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.1 mole) in 50 mL of water was added with stirring a solution of 17.6 g of 96% N,N'-Eten (0.2 mole) with 8.1 mL of 37%  $\text{HCl(aq)}$ , and 15.9 g of  $\text{NaNO}_2$  (0.23 mole) was added quickly. The mixture was stirred in an ice bath until dissolution. Next, 1 g of activated charcoal was added, (30) followed by the slow addition of 20 mL of 30%  $\text{H}_2\text{O}_2\text{(aq)}$ , with continual stirring. The mixture was stirred in the ice bath for 30 minutes, stirred at room temperature for 4 hours and was then heated on a steam bath for 1 hour. The mixture was evaporated to dryness at room temperature under an air

stream. The solid was successively triturated under 200 mL and 100 mL portions of methanol and filtered. The filtrate was evaporated to dryness, and then it was dissolved in 150 mL of water. To the aqueous solution was added dropwise with stirring a solution of 12.2 g of  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$  in 20 mL of water, and a single crop of ochre colored crystals was filtered. The crystals were washed successively with ethanol and ether and dried in vacuo. Yield: 6.30 g (14% of theory).

Air oxidation for 5-1/2 hours (2,19) to form the bis(N,N'-Eten) complex gave a vivid orange product, but in 10% yield. Again, 0.1 mole of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  was used as reactant.

The IR spectra of the  $[\text{Co(III)}(\text{N,N'-Meen})_2(\text{NO}_2)_2]\text{-ClO}_4$  complex had strong absorptions at 1320 and 1400  $\text{cm}^{-1}$ . The IR spectra of the  $[\text{Co(III)}(\text{N,N'-Et1pn})_2(\text{NO}_2)_2]\text{ClO}_4$  complexes had strong absorptions at 1320 and 1410  $\text{cm}^{-1}$ .

#### $[\text{Co(III)}(\text{N,N'-Eten})_2(\text{NO}_2)_2]^+$ Complex Resolution

The N,N'-Eten complex could not be resolved using (+)-silver- $\alpha$ -bromocamphor- $\pi$ -sulfonate monohydrate (AgBCS) by the method reported by Tiethof & Cooke for resolving the corresponding dinitrobis(N,N'-Meen) complex. (19) No diastereomeric precipitate could be ob-

tained from water, ethanol, n-propanol, n-butanol or sec-butanol. The solutions were each cooled to 6°C, 0°C and -12°C to try to induce crystallization, and the cooled beakers were scratched. The AgBCS was prepared by the method of Buckingham, Marzilli & Sargeson. (8)

### Conversion of $[\text{Co(III)}(\text{N,N}'\text{-Alkylen})_2(\text{NO}_2)_2]^+$ Complexes

#### Conversions with Hydrochloric Acid

##### Conversions to $[\text{Co(III)}(\text{N,N}'\text{-Alkylen})_2\text{Cl}_2]\text{ClO}_4$ .

Only  $[\text{Co(III)}(\text{N,N}'\text{-Meen})_2(\text{NO}_2)_2]\text{ClO}_4$  could be converted into the green trans-dichloro product using the method of Tiethof & Cooke. (19) This confirms the report of this conversion. (2,19) The corresponding dinitrobis-(N,N'-Eten) complexes with perchlorate and chloride counterions decomposed when attempting to prepare the corresponding trans-dichloro complexes.

##### Conversions to $[\text{Co(III)}(\text{N,N}'\text{-Alkylen})_2\text{NO}_2\text{Cl}]\text{ClO}_4$ .

Red chloronitro perchlorates were prepared for each bis-(N,N'-Alkylen) complex with N,N'-Meen and N,N'-Eten by the method of Buckingham, Marzilli & Sargeson. (17) Each of the chloronitro complexes,  $[\text{Co(III)}(\text{N,N}'\text{-Meen})_2\text{NO}_2\text{Cl}]\text{ClO}_4$  and  $[\text{Co(III)}(\text{N,N}'\text{-Eten})_2\text{NO}_2\text{Cl}]\text{ClO}_4$ , are new.

### Conversions with Hydrobromic Acid

Using a method equivalent to the method of Tiethof & Cooke (19) above, neither of the bis(N,N'-Meen) nor bis(N,N'-Eten) perchlorates or bromides yielded green trans-dibromo perchlorates or bromides. The bromide salts, like the chloride salts, had been obtained by passing the dissolved dinitro perchlorates through Dowex 1X-8 anion exchange resin in the bromide ion form. (2)

The conversion of 1.0 g of the known complex trans-[Co(III)(pn)(N,N'-Meen)(NO<sub>2</sub>)<sub>2</sub>]Cl (2) with 5 ml of 48% HBr(aq) at 60°C for 30 minutes yielded 0.54 g of an olive drab precipitate from a blood red solution on cooling to 20°C. The complex was presumably the chloronitro complex because of inner sphere coordination of the chloride counterion.

No reddish precipitates were obtained by a method equivalent to the method of Buckingham, Marzilli & Sargeson (8) above. Thus, neither bromonitro complex with N,N'-Meen or N,N'-Eten was obtained.

### Stability of Solid [Co(III)-(N,N'-Alkylen)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> Complexes

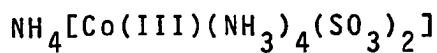
#### Complexes with bis(N,N'-Meen) Ligands

The solid dinitro and chloronitro complexes with perchlorate counterions were stable. The solid dinitro

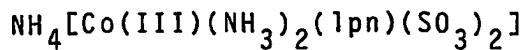
complexes with bromide and chloride counterions were stable. Samples were kept in plastic-stoppered vials.

#### Complexes with bis(N,N'-Eten) Ligands

The solid dinitro complexes with perchlorate and bromide counterions were stable. The solid dinitro complex with the chloride counterion slowly decomposed into a dark, glassy mass. The decomposition was first noticed about four months after its synthesis. The samples of the dinitro complexes were also kept in plastic-stoppered vials.



The complex was prepared by the method of Bailar & Peppard. (33) The total yield from 160 g of the reactant  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  was 141 g. The complex was assumed to be the trihydrate. (33)



The complex was prepared by the method of Saburi, Tsujito & Yoshikawa. (12) First, 7.3 g of 95% lpn was slowly added to a stirred suspension of 34 g of  $\text{NH}_4[\text{Co(III)}(\text{NH}_3)_4(\text{SO}_3)_2]$  in 500 mL of water. The resultant brown solution was stirred for approximately four hours, then evaporated to about half its original vol-

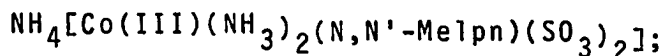
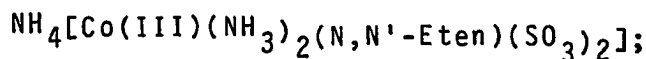
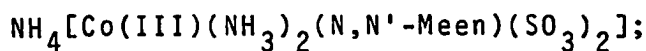
ume by an air stream, and filtered. To the evaporated filtrate was added an approximately equal volume of 95% ethanol which caused immediate precipitation. Tawny precipitates were suction filtered, washed successively with absolute ethanol, acetone and ether and were dried at 65°C. Yield: 25 g. Elemental analysis, calculated for  $\text{CoC}_3\text{H}_{20}\text{N}_5\text{S}_2\text{O}_6$ : C, 10.44%; H, 5.84%. Found: C, 10.85%; H, 6.08%.

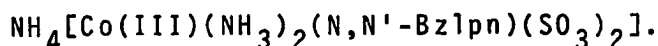
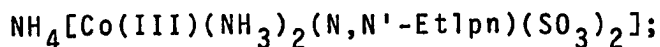
In a second preparation, the molar proportions of Saburi, Tsujito & Yoshikawa (12) were followed exactly. The second preparation was stirred for 3 hours and cooled to 6°C for precipitation.

#### New $\text{NH}_4[\text{Co(III)}(\text{NH}_3)_2(1,2\text{-diamine})(\text{SO}_3)_2]$ Complexes

New complexes with separate 1,2-diamines were prepared by following the molar proportions and method of Saburi, Tsujito & Yoshikawa (12) exactly and cooling to 6°C. The 1,2-diamines used were N,N'-Meen; N,N'-Eten; N,N'-Melpn; N,N'-Etlpn and N,N'-Bzlpn. Acetone addition caused further precipitation.

Five new  $\text{NH}_4[\text{Co(III)}(\text{NH}_3)_2(1,2\text{-diamine})(\text{SO}_3)_2]$  complexes were prepared. They were:





The IR spectra of each new complex showed the coordination of each of the 1,2-diamine ligands. The five new complexes were used as intermediates without purification in following indicated procedures.

trans-[Co(III)(NH<sub>3</sub>)<sub>2</sub>(1pn)Br<sub>2</sub>]Br

The complex was prepared by the method of Saburi, Tsujito & Yoshikawa. (12) The complex has been reported prepared by another method. (13)

In the first preparation of the complex in this work, 5.00 g of  $\text{NH}_4[\text{Co(III)}(\text{NH}_3)_2(1\text{pn})(\text{SO}_3)_2]$  (first preparation) was added to 15 mL of 48% HBr(aq) at 70°C, cooled, and stirred four hours. The dull green solid was filtered and washed with acetone. The yield was 0.70 g. A second crop was not obtained. Elemental analysis, calculated for  $\text{CoC}_3\text{H}_{16}\text{N}_4\text{Br}_3$ : C, 8.86%; H, 3.96%;. Found: C, 9.11%; H, 4.53%.

In a second preparation, 2.00 g of  $\text{NH}_4[\text{Co(III)}(\text{NH}_3)_2(1\text{pn})(\text{SO}_3)_2]$  (second preparation) was added to 8 mL of 48% HBr(aq) at 60°C, cooled, and stirred three hours. An air stream was blown across the surface of the liquid for the last hour. Bright green solids were collected by suction filtration and washed with ace-



tone. The yield was 0.30 g. The filtrate with acetone washings was cooled in ice, and a second crop was obtained of 0.69 g. Evaporation of this filtrate and cooling yielded a third crop which was of darker color. All crops were dried at about 65°C for approximately half an hour, totally yielding 1.36 g.

Elemental analysis, calculated for  $\text{CoC}_3\text{H}_{16}\text{N}_4\text{Br}_3$ : C, 8.86%; H, 3.96%; N, 13.77%. Found: C, 7.61%; H, 4.12%; N, 13.33%. The CD spectra (second preparation), in methanol (0.070%) showed the following specific ellipticities:  $-0.0065^\circ$  at 540 nm;  $+0.005^\circ$  at 640 nm, and the CD spectra in ethanol (0.037%) showed the following specific ellipticities:  $-0.065^\circ$  at 540 nm;  $0^\circ$  at 650 nm.

trans-[Co(III)(NH<sub>3</sub>)<sub>2</sub>(N,N'-Melpn)Br<sub>2</sub>]Br

In attempting to prepare the new complex, 0.19 g of  $\text{NH}_4[\text{Co(III)(NH}_3)_2(\text{N,N'-Melpn})(\text{SO}_3)_2]$  was added to 2 mL of 48% HBr(aq) at 60°C with stirring. The mixture turned green immediately with foaming, and the reaction was quickly cooled in an ice bath. (12) The mixture was stirred at room temperature for approximately 15 minutes and a fine yellow/green powder was collected by suction filtration, washed with acetone and dried at about 65°C for approximately one hour, yielding 0.28 g.

No further crop was obtained by the addition of acetone and cooling. The product could not be recrystallized from 2 N HBr(aq), (12) but it decomposed during the recrystallization attempts.

trans-[Co(III)(NH<sub>3</sub>)<sub>2</sub>(N,N'-Et1pn)Br<sub>2</sub>]Br

The method used for trans-[Co(III)(NH<sub>3</sub>)<sub>2</sub>(N,N'-Melpn)Br<sub>2</sub>]Br was used with 1.43 g of NH<sub>4</sub>[Co(III)(NH<sub>3</sub>)<sub>2</sub>(N,N'-Et1pn)(SO<sub>3</sub>)<sub>2</sub>] and 6 mL of 48% HBr(aq) in attempting to prepare the new complex. The first crop was 0.88 g. It was then washed with water and acetone to yield 0.13 g. Elemental analysis showed that the product was heavily contaminated, presumably with [Co(III)-(NH<sub>3</sub>)<sub>4</sub>Br<sub>2</sub>]Br. The desired product was not identified.

Other trans-[Co(III)(NH<sub>3</sub>)<sub>2</sub>(1,2-diamine)Br<sub>2</sub>]Br Complexes

The general method of Saburi, Tsujito & Yoshikawa (12) was used to attempt to prepare other new complexes. The other 1,2-diamines used were N,N'-Eten and N,N'-Bz1pn.

The NH<sub>4</sub>[Co(III)(NH<sub>3</sub>)<sub>2</sub>(N,N'-Bz1pn)(SO<sub>3</sub>)<sub>2</sub>] uniquely reacted with the HBr at room temperature. The others (including the attempted preparations with N,N'-Melpn and N,N'-Et1pn) required the usual heating to 60°C.

None of these complexes were recrystallized from

2 N HBr(aq) (12) or methanol. (13) All complexes decomposed upon the recrystallization attempts. No desired final products were identified.

trans-[Co(III)(NH<sub>3</sub>)<sub>2</sub>(1pn)Cl<sub>2</sub>]Cl

To prepare the new complex, 2.00 g of NH<sub>4</sub>[Co(III)-(NH<sub>3</sub>)<sub>2</sub>(1pn)(SO<sub>3</sub>)<sub>2</sub>] (second preparation) was mixed with 10 mL of 37% HCl(aq) at 60°C. The indigo mixture was allowed to evaporate to dryness at room temperature.

The glassy indigo solid was dissolved in about 50 mL of methanol and loaded onto a 3.5 cm diameter column containing 100 mL of Dowex 50W-X8 100-200 mesh cation exchange resin in the H<sup>+</sup> form in methanol. Elution with 0.3 N HCl (prepared from dry HCl gas) in methanol at a flow rate of from 1 to 2 mL per minute yielded a green band which was 2 cm wide when ready for collection 8 cm from the origin, and it was eluted and collected. A purple band containing the cis-dichloro isomers remained at the origin. (32) A portion of the green eluent was evaporated on a rotary evaporator at 35°C to dryness. A green solid of trans-[Co(III)(NH<sub>3</sub>)<sub>2</sub>(1pn)Cl<sub>2</sub>]Cl was collected, which turned slate-colored upon exposure to heat or ambient air.

Elemental analysis of a sample of the solid showed some contamination, presumably [Co(III)(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]Cl in

a 1:1 mole ratio. Calculated for  $\text{CoC}_3\text{H}_{16}\text{N}_4\text{Cl}_3 \cdot 2\text{HCl} \cdot \text{H}_2\text{O}$ : C, 9.89%; H, 5.53%; N, 15.37%. Found: N, 14.52%; C, 5.35%; H, 4.66%. The CD spectra in methanol (0.185% of a sample of the solid) showed specific ellipticities of  $-0.0065^\circ$  at 480 nm; and  $+0.0123^\circ$  at 610 nm.

$\text{trans-}[\text{Co(III)(NH}_3)_2(\text{N,N'-Meen})\text{Cl}_2]\text{Cl}$

A blue-green solid was initially prepared by the method used to prepare  $\text{trans-}[\text{Co(III)(NH}_3)_2(\text{lpn})\text{Cl}_2]\text{Cl} \cdot 2\text{HCl} \cdot \text{H}_2\text{O}$ , and it was similarly chromatographed. (32) The green band was collected in one 800-mL aliquot and was evaporated. The green product was readily converted into the purple cis- isomers under conditions similar to those used with the analogous lpn-complex.

$\text{trans-}[\text{Co(III)(NH}_3)_2(\text{N,N'-Eten})\text{Cl}_2]\text{Cl}$

A blue solid was initially prepared by the method for  $\text{trans-}[\text{Co(III)(NH}_3)_2(\text{lpn})\text{Cl}_2]\text{Cl} \cdot 2\text{HCl} \cdot \text{H}_2\text{O}$  and was similarly chromatographed. The green band presumably containing the  $\text{trans-}[\text{Co(III)(NH}_3)_2(\text{N,N'-Eten})\text{Cl}_2]\text{Cl}$  decomposed overnight on the resin into a steel grey-blue colored band. It was not otherwise collected.

Alternatively, 1.0 g of carbonatotetraaminecobalt-(III) chloride prepared by the method reported by Schlessinger & Roscow (34) was dissolved in 10 mL of

water, and 0.5 g of 96% N,N'-Eten was added. The solution was mixed with 12 mL of 37% HCl at 65°C. The mixture was maintained at 65°C. Bubbling occurred, but no trans- product was produced from the violet mixture.

### trans-[Co(III)L<sub>2</sub>Cl<sub>2</sub>]Cl Complexes

A series of trans-[Co(III)L<sub>2</sub>Cl<sub>2</sub>]Cl complexes were prepared with L a reactant 1,2-diaminopropane of

(a) racemic pn;

(b) a mixture of half racemic pn plus half lpn with  $[\alpha]_D^{20}$  of -34.2°; and

(c) lpn with  $[\alpha]_D^{20}$  of -34.2° exclusively.

Each preparation was by dropwise addition of the stoichiometric amount of L for a L to Co molar ratio of 2:1 to an ice-cold stirred solution of 5.95 g of cobalt(II) chloride hexahydrate in 20 mL of water. Next was added a small amount of activated charcoal to improve the yield, (30) and 1 mL of ether to control foaming. (29) Then 5 mL of ice-cold 30% hydrogen peroxide was added dropwise. (35) After the oxidation, 31.2 mL of 37% aqueous hydrochloric acid was used. (36) Finally, each mixture was evaporated to 30 mL, and one crop of each product was collected by filtration. Yields: (a), 2.7 g; (b), 2.5 g; (c), 2.0 g.

Elemental analysis was conducted of a sample of

complex (b), calculated for  $\text{CoC}_6\text{H}_{20}\text{N}_4\text{Cl}_3 \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$ : C, 18.67%; H, 6.53%; N, 14.51%; Co, 15.27%. Found: C, 18.56% $\pm$ 0.3%; H, 6.54% $\pm$ 0.2%; N, 14.52% $\pm$ 0.3%; Co, 15.4% $\pm$ 0.8%.

Sample (c) was recrystallized from ethanol at 60°C, cooling in ice. Yield: 1.1 g. A 0.5 g sample of complex (b) was recrystallized from 5 mL of ethanol at 60°C, cooling in ice. Yield: 0.18 g. In addition, a 0.5 g sample of complex (b) was recrystallized from 5 mL of methanol at 60°C, cooling in ice. Yield: 0.24 g.

Elemental analysis was conducted on a sample of the methanol-recrystallized sample of complex (b), calculated for  $\text{CoC}_6\text{H}_{20}\text{N}_4\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ : C, 20.59%; H, 6.91%; N, 16.01%; Co, 16.84%. Found: C, 20.5% $\pm$ 0.3%; H, 6.60% $\pm$ 0.3%; N, 16.19% $\pm$ 0.3%; Co, 16.9% $\pm$ 0.89%.

The CD spectra results are reported in the Results and Discussion section for the  $A_{1g} \rightarrow E_g$  transition measured at 610 nm. The CD spectra were taken in methanol.

### Chromatography

A similar preparation to the above using 1.95 g of 95% lpn, 2.98 g of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , and amounts of the other reagents proportional to these was carried out. The mixture was evaporated to dryness. The product was dissolved in 250 mL of methanol and loaded onto about

100 mL of Dowex 50W-X8 resin in the  $H^+$  form. The product of trans-[Co(III)(lpn)<sub>2</sub>Cl<sub>2</sub>]Cl was eluted with 0.3 N HCl in methanol. (32) The eluent was collected in two one-liter fractions, numbered 1 and 2 in the order of their collection.

Green products from each fraction were obtained by cooling each fraction, which had been evaporated to a point in slight excess of saturation at 30°C, in ice. A second crop, B, was obtained from each fraction by employing this method to each filtrate from the A crop. Yields: 1A, 0.24 g; 1B, 0.03 g; 2A, 0.12 g; 2B, 0.22 g. The PMR spectra of 1A and 2B were indistinguishable.

trans-[Co(III)L<sub>2</sub>Br<sub>2</sub>]Br

A series of trans-[Co(III)L<sub>2</sub>Br<sub>2</sub>]Br complexes were prepared with L a reactant 1,2-diaminopropane of

- (a) racemic pn;
- (b) a mixture of half racemic pn plus half lpn  
with  $[\alpha]_D^{20}$  of -34.2°; and
- (c) lpn with  $[\alpha]_D^{20}$  of -34.2° exclusively.

The complexes were prepared using 4.09 g CoBr<sub>2</sub>·6H<sub>2</sub>O as a reactant. The amounts of each L were sufficient for a L to Co molar ratio of 2:1. Each H<sub>2</sub>O<sub>2</sub>-oxidized mixture was evaporated to dryness and triturated with ethanol, filtering the peach colored tris- complexes. (37)

Each green ethanolic filtrate was evaporated to 125 mL, and a green crop of crystals was collected. Then the resultant filtrate was cooled in ice to collect a second green crop which was combined with the first. Yields: (a), 1.6 g; (b), 2.4 g; (c), 1.3 g.

Recrystallization of 0.5 g of (b) from 20 mL of boiling methanol and cooling in ice yielded 0.11 g. Recrystallization of 1.3 g of (c) from methanol yielded 0.4 g. The optical activity of the recrystallized (b) was lower than the optical activity of the originally prepared (b) complex.

#### Chromatography

A portion of the bromide complex (a) was dissolved in methanol and loaded onto a column of Dowex 50W-X8 in the  $H^+$  form in methanol. A green band was eluted with 0.3 N HBr in methanol by a method analogous to the method of LeMay & Aalbers. (32) The green complex of trans- $[Co(III)(pn)_2Br_2]Br$  was collected as a solid by filtration from the eluent.

#### Direct Methods to trans- $[Co(III)(1,2-dialkylaminoalkane)_2(Halo)_2]^+$ Complexes

No pure solid Co(III) complexes could be obtained by the  $H_2O_2$  oxidation (35,37) or air oxidation (36) of solutions of stoichiometric amounts of  $CoCl_2 \cdot 6H_2O$  or of



$\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$  in combination with any of the 1,2-dialkyl-aminoalkanes of N,N'-Melpn; N,N'-Eten or N,N'-Etlpn in a 1,2-dialkylaminoalkane to Co molar ratio of 2:1. The solvents used in each case were water, methanol and ethanol. Solids recovered were generally blue (cobalt(II)) and/or white (amine salt). The enantiomeric ligands were recovered from these solids.

#### Diamine Recovery

The N,N'-Etlpn and N,N'-Melpn ligands bound to cobalt complexes and the ligand salts from decomposed complexes were segregated as to species, placed under ether and cooled in an ice bath. To the volume of coordinated ligands and ligand salts was added an equivalent volume of sodium hydroxide pellets. The compounds were intimately mixed by careful stirring. A small quantity of water was added with stirring, and after the reaction had subsided, the ethereal solution was decanted. The alkalized mixture was again submersed under ether, and a small fresh amount of sodium hydroxide was added. The compounds were again stirred, and the ethereal solution was decanted. The decantates were filtered, reduced in volume and distilled over a few potassium hydroxide pellets. The distillation system was vented through anhydrous calcium sulfate drying tubes.

The recovery of N,N'-Etlpn was more efficient.

Yields of recovered N,N'-Et1pn were about 50% of theory. The head temperature of recovered N,N'-Et1pn was 153-156°C. Yields of recovered N,N'-Me1pn were about 30% of theory.

## CHAPTER IV

### RESULTS AND DISCUSSION

#### (R)-1,2-Diaminopropane and Its Derivatives

##### Distillation and Resolutions of (R)-1,2-Diaminopropane

##### Method With (+)-Tartaric Acid

In this work, (R)-1,2-diaminopropane was obtained in high concentration and in good yields without the use of alkali metals in distillation. Directly combining the dry dihydrochloride salt of lpn and excess dry solid potassium hydroxide enabled the achievement of the high aqueous concentration, which exceeded 95% by weight. The yields from the dry lpn·2HCl were good, about 90% of theory.

The preparation of optically pure lpn has been studied by numerous other workers. The original method of Baumann, (38) who recrystallized the hydrogen (+)<sub>D</sub>-tartrate in water, has been the basis for many later methods of resolving lpn from racemic pn. To obtain the lpn boiling at 120°C, Baumann (38) and Tschugaeff & Sokoloff (39,40) used sodium metal in each of their distillations of lpn after the lpn was freed from the (+)<sub>D</sub>-tartrate with KOH and barium oxide. However, it should

be noted that distillation with the tartrate in the pot has the drawback of causing foaming which results in lower yields in the distillation. (21)

Thus, in the preparation of lpn, the foam-causing lpn·(+)<sub>D</sub>-tartrate diastereomer salt is usually converted by most workers to the dihydrochloride salt with potassium chloride by the method of Bailar, Jonassen & Gott, (22) which procedure was followed in this work. Bailar, Jonassen & Gott (22) reported collecting a distillate of aqueous lpn 80% by weight by converting a concentrated aqueous solution of the lpn·2HCl to lpn by adding solid potassium hydroxide and distilling. Tiethof (2) reported only 35% lpn from following the method of Bailar, Jonassen & Gott. (22) Dwyer, Garvan & Shulman (21) reported distilling aqueous lpn 67% by weight after freeing the lpn from solid lpn·2HCl with sodium hydroxide flakes and distilling with the sodium hydroxide in the pot.

In this work, (R)-1,2-diacetamidopropane was to be prepared from the reaction of acetic acid with lpn. In order to minimize the presence of excess water and increase the efficiency of the preparation of the (R)-bisamide, lpn of a higher concentration was desirable, although it was not desired to use distillation methods requiring sodium metal to prepare anhydrous lpn because a certain amount of water is produced by the N-acetyla-

tion with acetic acid.

In this work, following the distillation method of Bailar, Jonassen & Gott (22) exactly, the lpn produced was of an aqueous concentration of less than 80% by weight (35-75%). Mixing moist  $\text{lpn} \cdot 2\text{HCl}$  with solid KOH yielded lpn in 85% concentration. As stated above, the water content of the lpn produced in this work was reduced to less than 5% by combining dry  $\text{lpn} \cdot 2\text{HCl}$  with the threefold excess of KOH by volume and distilling in a dry system. In addition, in this work preliminary trial distillations with sodium hydroxide flakes produced lpn of a lower concentration (60%) such as the lpn produced by Dwyer, Garvan & Shulman (67%): (21) From the results of these other workers (21,22) and from the results of this work, it can be seen that the excess KOH binds the water produced in freeing the lpn from the  $\text{lpn} \cdot 2\text{HCl}$  more effectively in the distillation pot than does NaOH.

Dwyer, Garvan & Shulman (21) improved upon the method of Baumann, (38) by resolving lpn with multiple recrystallizations with (+)<sub>D</sub>-tartaric acid from diminishing volumes of acetic acid in water. After ten recrystallizations, Dwyer, Garvan & Shulman (21) obtained lpn with  $[\alpha]_D$  in dry benzene of  $-34.2^\circ$ , and after twenty-three recrystallizations they improved the specific rotation to  $-34.8^\circ \pm 0.4^\circ$ . They considered

ten recrystallizations sufficient and considered  $-34.8^\circ$  in dry benzene as the specific rotation of the pure enantiomer. (21)

By following the resolution method of Dwyer, Garvan & Shulman (21), the optical quality of the lpn obtained with (+)<sub>D</sub>-tartaric acid in this work was high. The specific rotation at 589 nm of the lpn in dry benzene obtained herein was greater than or equal to  $|-34.2^\circ|$ .

#### Method with Cobalt Complexes

The partial resolution of pn to obtain lpn with  $[\alpha]_D$  of  $-11.5^\circ$  using tris-cobalt(III) complexes has been reported by Dwyer, Garvan & Shulman. (21)

In this work, study of the change in optical activity of the trans-[Co(III)L<sub>2</sub>X<sub>2</sub>]X complex made with 50% lpn/50% pn and X of Cl<sup>-</sup> or Br<sup>-</sup> showed that the optical activity of the trans-[Co(III)L<sub>2</sub>Cl<sub>2</sub>]Cl complex improved with recrystallization from methanol and ethanol. Recrystallization from methanol gave the better improvement (61% improvement from methanol vs. 10% improvement from ethanol).

Because each 1,2-diaminopropane enantiomer orients stereospecifically on trans-cobalt complexes such as on these trans-[Co(III)L<sub>2</sub>X<sub>2</sub>]X complexes, (11) optical activity of the complex can be related to optical ac-

tivity of the 1,2-diaminopropane. (21) The trans- $[\text{Co(III)(pn)}_2\text{X}_2]^+$  complexes with racemic pn are optically inactive. The trans- $[\text{Co(III)(lpn)}_2\text{X}_2]^+$  complexes are optically active. (1) The trans- $[\text{Co(III)N}_4\text{X}_2]^+$  complexes with two of the planar  $\text{N}_4$  sites chelated by one lpn and the other two  $\text{N}_4$  sites chelated by optically inactive ligands have optical activity in the  $\text{A}_{1g} \rightarrow \text{E}_g$  transition half the value of the trans- $[\text{Co(III)(lpn)}_2\text{Cl}_2]^+$  complex. (1,2,13,15)

Optical activity intermediate between the extremes of the bis(pn) and bis(lpn) trans- $[\text{Co(III)L}_2\text{X}_2]^+$  complexes was obtained for the 1,2-diaminopropane ligand mixture of 50% lpn/50% pn. The optical activity of trans- $[\text{Co(III)L}_2\text{Cl}_2]\text{Cl}$ , measured by the  $\text{A}_{1g} \rightarrow \text{E}_g(\text{D}_{4h})$  transition appearing in the CD spectra, improved with recrystallization, as Table 1 shows. However, Table 1 also shows that the initial formation of the trans- $[\text{Co(III)L}_2\text{Cl}_2]\text{Cl}$  complex resulted in a mixed 1,2-diaminopropane ligand coordinated to Co(III) with a lower optical activity than 50% lpn/50% pn was expected to provide ( $\Delta\epsilon$ , +0.35). (41) This may be related with the increased production of trans- $[\text{Co(III)(pn)}_2\text{Cl}_2]\text{Cl} \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$  (2.7 g) compared to trans- $[\text{Co(III)(lpn)}_2\text{Cl}_2]\text{Cl} \cdot \text{HCl} \cdot 2\text{H}_2\text{O}$  (2.0 g), as each complex was produced from 6 g of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ . However, a statistically significant number of recrystallization preparations such as

the ones from this work has not been carried out, and the immediately foregoing production relationship cannot be made with certainty. The work of Corey & Bailar (41) suggests that each enantiomer, trans-[Co(III)(l<sub>pn</sub>)<sub>2</sub>Cl<sub>2</sub>]Cl and trans-[Co(III)(d<sub>pn</sub>)<sub>2</sub>Cl<sub>2</sub>]Cl, are produced in amounts nearly equivalent to the ratio of l<sub>pn</sub> to d<sub>pn</sub> and that each enantiomer has the same solubility characteristics. Recrystallization can be used, of course, to selectively remove a minority component of a mixture, which trans-[Co(III)(d<sub>pn</sub>)<sub>2</sub>Cl<sub>2</sub>]Cl is in the complex, trans-[Co(III)L<sub>2</sub>Cl<sub>2</sub>]Cl with L a mixture of pn and l<sub>pn</sub>. However, such trans-[Co(III)-(d<sub>pn</sub>)<sub>2</sub>Cl<sub>2</sub>]Cl removal to obtain trans-[Co(III)(l<sub>pn</sub>)<sub>2</sub>-Cl<sub>2</sub>]Cl also removes the desired bis(l<sub>pn</sub>) complex. Thus, the method of recrystallizing trans-[Co(III)-L<sub>2</sub>Cl<sub>2</sub>]Cl is not very effective for resolving l<sub>pn</sub>, even with methanol recrystallization. Table 1 follows.



Table 1

The  $A_{1g} \rightarrow E_g$  CD Spectra of trans-[Co(III)L<sub>2</sub>Cl<sub>2</sub>]Cl

Sample Identity	Molar ellipticity ( $\Delta\epsilon$ )
<u>trans</u> -[Co(III)(50% lpn/50% pn) <sub>2</sub> Cl <sub>2</sub> ]Cl	
First Crop	+ 0.23
Recrystallized from ethanol	+ 0.25
Recrystallized from methanol	+ 0.37
<u>trans</u> -[Co(III)(lpn) <sub>2</sub> Cl <sub>2</sub> ]Cl	
Recrystallized from ethanol	+ 0.7

Elemental analyses were conducted of the trans-[Co(III)L<sub>2</sub>Cl<sub>2</sub>]Cl complexes to help insure that the observed increase in optical activity was not due merely to removal of other impurities besides the less optically active complex. These elemental analyses do support, though, the increased resolution of lpn from the partially resolved 1,2-diaminopropane ligand with trans-[Co(III)L<sub>2</sub>Cl<sub>2</sub>]Cl complexes, after the initial complex is formed. However, the yields from the recrystallization prohibit the practical use of the trans-[Co(III)L<sub>2</sub>Cl<sub>2</sub>]Cl resolution. The methanol recrystallization of trans-[Co(III)L<sub>2</sub>Br<sub>2</sub>]Br resulted in decreased optical activity. This decreased optical activity from simple methanol recrystallization shows why

other workers such as Hawkins, Lawrance & Peachey (37) do not employ such a simple methanol recrystallization, but instead, precipitate the trans-[Co(III)(l<sub>pn</sub>)<sub>2</sub>Br<sub>2</sub>]Br from methanol by using the addition of ether.

The trans-[Co(III)L<sub>2</sub>Cl<sub>2</sub>]Cl complex resolution of partially resolved pn was not nearly as effective as the recrystallization of the (+)<sub>D</sub>-tartrate diastereomer with l<sub>pn</sub>. It is, practically speaking, of little utility in comparison to the resolution of pn with the (+)<sub>D</sub>-tartrate, which efficiently and dependably resulted in l<sub>pn</sub> with  $[\alpha]_D \geq |-34.2^\circ|$  in dry benzene.

#### Solid (R)-1,2-Diaminopropane Optical Purity Derivatives

The specific rotation of l<sub>pn</sub> in dry benzene is not the only quoted criterion of optical purity of the pn enantiomer. The specific rotation of free l<sub>pn</sub> distilled once over sodium had been used by Baumann (38) and Tschugaeff & Sokoloff. (39,40) However, the variation in specific rotation depends on the hygroscopic nature of l<sub>pn</sub> and the change in sign that accompanies protonation. (21) Truly anhydrous (blue) l<sub>pn</sub> requires a procedure which involves several distillations over sodium and potassium. (42) Thus, the specific rotation of free l<sub>pn</sub> is not usually used as a criterion of optical purity. The specific rotation of the dihydrochloride salt in water of +3.99° to +4.10° has been

quoted as another criterion of optical purity of lpn. (22) However, the small rotation of  $\text{lpn} \cdot 2\text{HCl}(\text{aq})$  is too low to be of practical use. (21) The melting point of  $142^\circ\text{C}$  for the  $\text{lpn} \cdot (+)_D$ -tartrate diastereomer salt has been quoted as another criterion of optical purity of lpn. (43) However, the melting point of the diastereomer salt is unreliable because of the decomposition near it. (21) Values from  $141^\circ\text{C}$  to  $143^\circ\text{C}$  have been reported. (38,39) Such melting point values were obtained for the  $\text{lpn} \cdot (+)_D$ -tartrate diastereomer salt in this work ( $141$ - $144^\circ\text{C}$ ).

What would be desirable is a dependable solid derivative of lpn which can be used as an index of the optical purity of the enantiomer. (R)-1,2-Diacetamidopropane, prepared from lpn in this work, is such a solid derivative.

Reihlen, Weinbrenner & Hessling (4) prepared (R)-1,2-diacetamidopropane from (R)-2-acetyl-1-alaninonitrile with acetic anhydride. The (R)-1,2-diacetamidopropane prepared by the method of Reihlen, Weinbrenner & Hessling (4) was reported to melt at  $153^\circ\text{C}$ . The (R)-1,2-diacetamidopropane made from optically pure lpn would also be expected to melt at the same point, of course.

In this work, (R)-1,2-diacetamidopropane made from lpn with  $[\alpha]_D^{25}$  of  $-34.3^\circ$  melted at  $153.5^\circ\text{C}$ . This

melting point is well away from the 140°C melting point of racemic 1,2-diacetamidopropane (43,44) and is within experimental error of the melting point of the (R)-bisamide reported by Reihlen, Weinbrenner & Hessling. (4) The racemic bisamide is often quoted as a dependable characterization derivative of pn. No decomposition was observed near the (R)-1,2-diacetamidopropane melting point. Thus, (R)-1,2-diacetamidopropane prepared from lpn can be used to help check the optical purity of the lpn.

Other characterizing evidence in this work further supported the existence of (R)-1,2-diacetamidopropane. The carbon analysis of (R)-1,2-diacetamidopropane was within 0.65% of theoretical with the m.p. sharp, within 0.5°C, which indicates a pure compound. The IR spectra of (R)-1,2-diacetamidopropane was equivalent to the IR spectra of racemic 1,2-diacetamidopropane. The strong  $1640\text{ cm}^{-1}$  absorption and the  $1650\text{ cm}^{-1}$  shoulder in the IR spectra were assigned to be from amide carbonyl stretching, the  $3280\text{ cm}^{-1}$  absorption from secondary amide N-H stretching and the  $1550\text{ cm}^{-1}$  absorption from N-H bending. (45) (R)-1,2-diacetamidopropane consistently melted at the higher temperature of 153.5°C. (4) The racemic 1,2-diacetamidopropane made by the corresponding process of reacting pn with acetic acid melted at its accepted value. (43,44)

### (R)-1,2-Diethylaminopropane

The new 1,2-diamine, (R)-1,2-diethylaminopropane, was prepared through lithium aluminum hydride reduction of (R)-1,2-diacetamidopropane. Yields of N,N'-Et1pn from the reduction of the (R)-bisamide were good, about 54% of theory. Yields of (R)-1,2-diacetamidopropane from 1pn and glacial acetic acid (molar ratio of 1pn to acid, 1.0:2.1) were also good, over 60% of theory in which 95% 1pn was used. Thus, the overall yields from 1pn were acceptable. Alkalizing and slightly wetting the quenched reducing agent helped free more N,N'-Et1pn and helped to improve the yields. Combining smaller batches into larger batches for the distillation also helped improve yields to 60% of theory based on the (R)-bisamide.

Rice, Armbrecht, Grogan & Reid (25) reported that lithium aluminum hydride reduction of 1,2-diacetamidoethane yielded 1,2-diethylaminoethane. The N,N'-Eten was obtained in their work at 50% yield from the reduction and was collected at 148-150°C. (25)

The boiling point of en is 116.5°C, (44) and the boiling point of 1pn is 121°C. (40) The boiling point of N,N'-Meen is 120.5°C, (44) and Tiethof (2) collected N,N'-Melpn at 125.5-129°C. Thus, it can be seen that the C-methyl group of 1pn and its N,N'-alkyl deriva-

tives contributes approximately 5-6°C to the boiling point of en and its N,N'-alkyl derivatives. Thus, when compared to the 148-150°C boiling point of N,N'-Eten, the boiling point of N,N'-Etlpn might be expected to be found at 153-156°C.

In this work, N,N'-Etlpn was consistently collected at 153-156°C. The 153-156°C boiling point was found for the freshly prepared N,N'-Etlpn and for the N,N'-Etlpn recovered from cobalt complexes.

Other characterizing evidence confirmed the compound. It was prepared from a closely analogous reduction known to produce N,N'-Eten. (25)

The dihydrochloride salt of N,N'-Etlpn yielded a carbon analysis within 0.7% of theoretical, which is acceptable. The new 1,2-diamine, N,N'-Etlpn, was characteristically basic, and it was soluble in water, methanol and ethanol in a manner similar to its N,N'-Alkyl homolog, N,N'-Melpn. The PMR spectra of the N,N'-Etlpn ligand coordinated in dinitro cobalt(III) complexes showed a quartet from 3.05-3.12 ppm which was attributed to methylene protons adjacent to an amino nitrogen and split by 3 protons attributed to a methyl group adjacent to the methylene moiety. (46) Its smell was characteristic of lower N-alkylated amines. It also showed an anorectic effect characteristic of similar amines. (47)

### Optical Activity of (R)-1,2-Dialkylaminopropanes

(R)-Diethylaminopropane, like (R)-1,2-diaminopropane, was levorotary at 589 nm in dry benzene with  $[\alpha]_D^{20}$  of  $-59^\circ$  (0.01 g/10 mL). The levorotary optical activity of N,N'-Etlpn is more pronounced than, but of the same sign as, the other (R)-1,2-dialkylaminopropane studied in this work, (R)-1,2-dimethylaminopropane.

The  $[\alpha]_D$  of 0.07 g of N,N'-Melpn per 10 mL of dry benzene has been reported to be  $-48.5^\circ$ . (3) However, the N,N'-Melpn used to obtain this specific rotation was prepared from lpn with  $[\alpha]_D$  of  $-33.2^\circ$ . (2) The  $[\alpha]_D^{25}$  of 0.15 g of the N,N'-Melpn prepared in this work per 10 mL of dry benzene was  $-53.6^\circ$ . The N,N'-Melpn prepared in this work was prepared from lpn with higher enantiomeric purity ( $[\alpha]_D^{25}$  of  $-34.3^\circ$ ) than the other reported N,N'-Melpn. (2) Each preparation of N,N'-Melpn, which was prepared formerly (2) and prepared in this work, was by the same method. (2)

The difference in concentrations may be a cause of part of the difference in reported specific rotations. Both measurements were taken in dry benzene at concentration levels below 0.2% by weight. Thus, each measurement was taken at a molar concentration of about 0.01 to 0.02 M.

Dwyer, Garvan & Shulman (21) reported that the specific rotation of lpn in dry benzene is independent of concentration between the range of 0.53% to 2.84%, which is between the range of about 0.05 M to 0.3 M. The optical measurements taken of N,N'-Melpn were outside this range. However, it has not been reported if a concentration dependence for lpn below 0.05 M exists, or if it does, how it deviates from linearity. Still, the concentration difference from this linear range of lpn with the two N,N'-Melpn measurements is not so great as to be alarming and is not conclusive of an unreasonable comparison.

In addition, if lpn with  $[\alpha]_D$  of  $-33.2^\circ$  prepares N,N'-Melpn with  $[\alpha]_D$  of  $-48.5^\circ$  and if a linear relationship is assumed between the specific rotation of lpn and the N,N'-Melpn prepared from it by the method of Tiethof, (2) optically pure lpn with  $[\alpha]_D$  of  $-34.8^\circ$  should similarly prepare N,N'-Melpn with  $[\alpha]_D$  of  $-50.9^\circ$  at the same concentration of 0.07 g per 10 mL of dry benzene.

Considering the foregoing, the specific rotation of N,N'-Melpn in dry benzene is probably concentration dependent. An  $[\alpha]_D$  value of  $-52^\circ$  at a concentration of 0.1 g per 10 mL of dry benzene is a reasonable expectation for the optically pure enantiomer of N,N'-Melpn at room temperature.



Similarly, the specific rotation of N,N'-Et1pn prepared in this work was measured at a low concentration. An  $[\alpha]_D$  value of  $-60^\circ$  at a concentration of 0.1 g per 10 mL of dry benzene is a reasonable expectation for the optically pure enantiomer of N,N'-Et1pn, adjusting for the concentration at the measurement.

#### (R)-1,2-Dibenzylaminopropane

The new 1,2-diamine, (R)-1,2-dibenzylaminopropane, was prepared in this work both from the lithium aluminum hydride reduction and from the sodium borohydride reduction of the Schiff's base reaction product of benzaldehyde and 1pn in a benzaldehyde to 1pn molar ratio of 2:1. (27,28,29) The product was not completely characterized primarily because the interest in coordinating such a ligand onto trans- $[\text{Co(III)}\text{N}_4\text{X}_2]^+$  complexes waned when, in this work, pure trans- $[\text{Co(III)}(\text{NH}_3)_2(\text{N,N}'\text{-Bzl1pn})\text{Br}_2]\text{Br}$  could not be prepared from the new intermediate  $\text{NH}_4[\text{Co(III)}(\text{NH}_3)_2(\text{N,N}'\text{-Bzl1pn})(\text{SO}_3)_2]$ , and difficulties were encountered in complexing the less unstable N,N'-Et1pn onto other trans- $[\text{Co(III)}\text{N}_4\text{X}_2]^+$  complexes as well.

However, the N,N'-Bzl1pn distilled at a temperature close to the  $222^\circ\text{C}$  (reduced pressure) head temperature of 1,2-dibenzylaminoethane reported by Van Alphen. (27, 28) The N,N'-Bzl1pn in this work distilled at about

260°C, but distilled over a wide range of about 40°C. It was immiscible in water, was yellow, oily and had a fishy, characteristic amine odor. It was levorotary at the sodium D-line and the mercury green line. It seemed to have an anorectic effect on human physiology which was greater than that of N,N'-Et1pn, which is characteristic of similar amines. (47)

The dibenzoyl derivative of 1pn prepared by the method of Shriner, Fuson, Curtin & Morrill (23) could not be reduced by lithium aluminum hydride to N,N'-Bz1pn. The attempted reaction was carried out in an ether slurry for 10 hours at reflux. The dibenzoyl derivative was too stable to such  $\text{LiAlH}_4$  treatment to prepare the N,N'-Bz1pn by this latter method.

#### Storage and Handling

Storage of the free 1,2-diamines in glass bottles with greased ground glass stoppers avoided some laboratory problems common to free 1,2-diamines. Permeation of vapors through cork and rubber stoppers and commercial plastic caps was one such problem. By using greased ground glass equipment, reaction of the free 1,2-diamines with atmospheric water vapor and carbon dioxide was minimized and so was the presence of the 1,2-diamine vapor in the laboratory air. Another problem avoided was reaction of the 1,2-diamine with

the stoppers themselves, which would have degenerated the stopper and contaminated the 1,2-diamine.

Due caution was exercised in handling the new 1,2-diamine, N,N'-Et1pn, in a manner similar to the other known 1,2-diamines. It had a noticeable anorectic effect, and thus, like other amines, it was considered active with the central nervous system. (47) Because it was enantiomeric, its physiological effects may have differed from the racemate or its antipode. N,N'-Et1pn was volatile and flammable.

The new 1,2-diamine, N,N'-Bz1pn, was also handled with due caution. It also seemed to have an anorectic effect on the human physiology. It was not as volatile as N,N'-Et1pn or the other lower molecular weight 1,2-diamines.

### Cobalt(III) Complexes

#### [Co(III)(N,N'-Et1pn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>] Complexes

The positional isomers trans,trans- and trans,-cis-dinitrobis((R)-1,2-diethylaminopropane)cobalt(III) with accompanying monovalent counterions were prepared, but in low quantities and contaminated with salts. The positional isomers are illustrated in Figure 7.

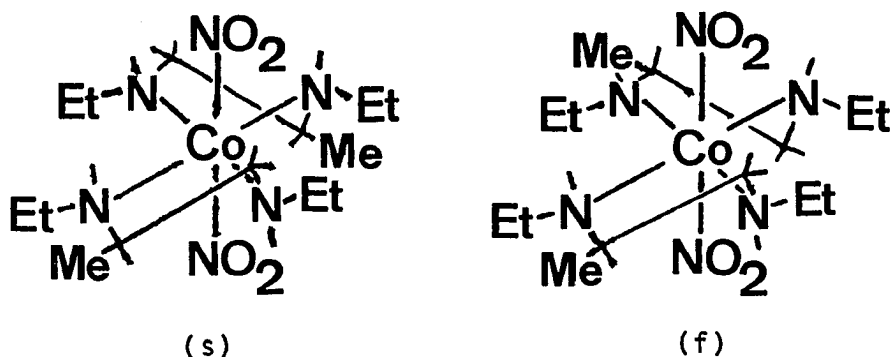


Figure 7. Positional Isomers of  $\text{trans-[Co(III)(N,N'-Et1pn)}_2(\text{NO}_2)_2]^+$ . The trans,trans- isomer (s) is on the left, and the trans,cis- isomer (f) is on the right. The positional isomerism refers to the C-methyl group of the  $\lambda$ -chelate rings.

The  $[\text{Co(III)(N,N'-Et1pn)}_2(\text{NO}_2)_2]^+$  complexes were prepared with the counterions of bromide, chloride and perchlorate, and the trans- positional isomers were separated from each other by apportioning the one trans-band into two fast (f), one medium (m) and two slowly (s) eluting fractions, by the method Tiethof & Cooke (3) reported for the preparation and separation of the corresponding complexes made with N,N'-Melpn. The trans- $[\text{Co(III)(N,N'-Et1pn)}_2(\text{NO}_2)_2]^+$  complexes presumably could not be prepared in enough yield to separate them as pure complexes from contaminating salts after their chromatographic resolution with Dowex 50W-X8 cation exchange resin in the ammonium ion form.

The UV-visible spectra of  $[\text{Co(III)(1,2-diamine)}_2-$

$(\text{NO}_2)_2]^+$  complexes is recognized as indicative of the presence of cis- or of trans-dinitro complexes. (12) The  $[\text{Co(III)}(1,2\text{-diamine})_2(\text{NO}_2)_2]^+$  complexes show a UV-visible spectra absorption maximum near 330 nm for the cis- isomers and near 345-350 nm for the trans- isomers. (12) In this work, the UV-visible spectra of a sample of the one trans- band removed by suction hose (If fraction) showed a maximum absorption at 343 nm ( $29,000 \text{ cm}^{-1}$ ), which indicated that the identity of the one trans- band was indeed of the trans- isomers of  $[\text{Co(III)}(\text{N,N'-Etlpn})_2(\text{NO}_2)_2]^+$ . The UV-visible spectra of trans- $[\text{Co(III)}(\text{N,N'-Etlpn})_2(\text{NO}_2)_2]^+$  prepared in this work resembled the UV-visible spectra of other trans- $[\text{Co(III)}(1,2\text{-diamine})_2(\text{NO}_2)_2]^+$  complexes prepared by other workers, as well, such as trans,trans- $[\text{Co(III)}(\text{N,N'-Melpn})_2(\text{NO}_2)_2]^+$  ( $\lambda_{\text{max}}, 28,700 \text{ cm}^{-1}$ ) (2) and trans- $[\text{Co(III)}(\text{N,N'-Medpn})_2(\text{NO}_2)_2]^+$  ( $\lambda_{\text{max}}, 29,000 \text{ cm}^{-1}$ ). (12)

The trans- complexes were assigned as having  $\lambda$ -chelate rings with equatorial N,N'-diethyl groups because of the chromatographic elution, UV-visible spectra and CD spectra resemblance to the trans- $[\text{Co(III)}(\text{N,N'-Melpn})_2(\text{NO}_2)_2]^+$  isomers reported by Tiethof & Cooke, (3) which were assigned as having  $\lambda$ -chelate rings. Both N,N'-Etlpn and N,N'-Melpn were prepared from lpn without the breaking of bonds to the

chiral carbon in lpn, and thus, both N,N'-Etlpn and N,N'-Melpn have (R)-configurations about the chiral carbon. These 1,2-diamine ligands, like lpn, are assumed to orient on cobalt stereospecifically, (10) and Tiethof (2) showed by the analysis of a series of compounds using CD spectra that the N,N'-Melpn in his work indeed oriented stereospecifically in the  $\lambda$ -configuration. The  $\lambda$ -chelate ring configuration assignment in this work is also supported by the CD spectra resemblance of the trans-[Co(III)(N,N'-Etlpn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> complexes to the mirror image of the CD spectra of trans-[Co(III)(N,N'-Medpn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> reported by Saburi, Tsujito & Yoshikawa. (12) Saburi, Tsujito & Yoshikawa (12) assigned  $\delta$ -conformation chelate rings to the trans-dinitrobis(N,N'-Medpn)Co(III) complex they prepared.

The s fractions in this work contained the trans,-trans-[Co(III)(N,N'-Etlpn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> isomer, and the f fractions contained the corresponding trans,cis- isomer. The m band contained both isomers. The positional isomers were assigned based on the assignment of Tiethof & Cooke, (3) who assigned the trans,trans-[Co(III)-(N,N'-Melpn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> positional isomer to be in the slower eluting portions of the trans- band eluted with the dilute NaClO<sub>4</sub> (aq). In this work, the same method was used for the resolution of trans-[Co(III)(N,N'-Etlpn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> positional isomers as was carried out by

Tiethof to resolve the positional isomers of the analogous trans-[Co(III)(N,N'-Melpn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> complex. (2)

The separation of trans-[Co(III)(N,N'-Etlpn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> into two different isomeric complexes in this work had visible support by the different stability characteristics each isomer fraction showed after resolution. Imbedded in salts which contained sodium chloride, the Is and IIs (chloride counterion and chloride/perchlorate counterion) trans- bands began to visibly turn green from decomposition within a few weeks after resolution. The If and IIf (chloride counterion) trans- bands were still orange/yellow after several months, but close inspection showed some green specks. The If and IIf (chloride counterion) trans- bands retained their overall yellow/brown color for well over 10 months. The m (chloride counterion) band was intermediate in this characteristic, turning visibly green by speckling after a month and taking five or six months to become primarily green.

The trans,trans- isomer presumably had a higher entropic factor than the trans,cis- isomer, and concerted vibration and stretching along the N'-Co-N' axis of the trans,trans- isomer is believed to have contributed to the faster decomposition of the s fractions. The conformationally labile N- and N'-ethyl groups presumably provided more strain on the Co-N bonds from their move-

ments than did the N- and N'-methyl groups on the trans-dinitro complexes with chloride counterions prepared by Tiethof (2) and by Saburi, Tsujito & Yoshikawa, (12) none of which were reported to decompose as solids.

The PMR spectra of the IIf fraction showed the presence of the paramagnetic cobalt(II) ion from the decomposition, as peak broadening occurred. (46) The paramagnetic decomposition product was filtered, and a more useful PMR spectra was obtained of the trans,cis-complex. Because of the insolubility of the decomposition product in water, it was proposed to have polymeric links. Cobalt is known to be catalytic in the condensation oligimerizations of en and tn. (48) The PMR spectra of  $[\text{Co(III)(N,N'-Et1pn)}_2(\text{NO}_2)_2]\text{NO}_3$  did not show any paramagnetic cobalt(II) interference.

Tiethof (2) has indicated that the PMR spectra is not the most sound indicia of trans,trans- and trans,cis- isomerism of the trans- $[\text{Co(III)(N,N'-Me1pn)}_2\text{X}_2]^+$  type complexes, but in this work, the PMR spectra was most useful to show coordination of the ligands of (R)-1,2-diethylaminopropane in the complex. The PMR spectra of the IIf fraction, rechromatographed mixture of If and IIf fractions and the nitrate counterion complexes of  $[\text{Co(III)(N,N'-Et1pn)}_2(\text{NO}_2)_2]^+$  each showed a quartet from 3.05-3.12 ppm which was assigned as arising from the protons of the N-methylene groups of the com-



plexed N,N'-EtIpn. (46) The N-methylene signal was split into a quartet from the three adjacent methyl protons which were on the N-ethyl groups. Because the spectra were taken in neutral D<sub>2</sub>O, the secondary amino hydrogens were deuterated rapidly and the methylene quartet was not further split. (1) No N-H peaks were observed. The signals arising from the methyl groups on the trans,cis- chromophore were complex and were found overlapped from 1.2-1.5 ppm. (12)

Elemental analysis of the If fraction indicated major contaminants were sodium perchlorate and sodium chloride. The elemental analysis also showed that water and finally, ammonium perchlorate and ammonium chloride were present, which was confirmed by the PMR spectra. The PMR spectra of the chromatographed IIf fraction and the rechromatographed mixture of If and IIf fractions showed the broad water band covering from 4.6-4.8 ppm and strong ammonium ion peaks at 6.7, 6.9 and 7.1 ppm. (46) The PMR spectra of the nitrate counterion complex, which was not chromatographed, did not show the ammonium ion peaks.

The IR spectra of the If and IIf trans- band fraction complexes each showed a strong absorption around 1400 cm<sup>-1</sup>. The presence of a solitary IR spectra absorption in the vicinity near 1300-1400 cm<sup>-1</sup> is consistent with the presence of the trans-dinitro groups in

the complex as reported by Goto, Okubo, Sawai & Yoshikawa. (49) Before the chromatography, the complexes had an additional absorption in the IR spectra around  $1320\text{ cm}^{-1}$  which is indicative of the presence of a cis-dinitro complex. (49) The nitrate counterion complex of  $[\text{Co(III)}(\text{N,N'-EtIpn})_2(\text{NO}_2)_2]^+$  was not chromatographed. It had a  $1320\text{ cm}^{-1}$  IR spectra absorption about half the intensity of its  $1390\text{ cm}^{-1}$  absorption. The IR spectra of unchromatographed  $[\text{Co(III)}(\text{N,N'-Eten})_2(\text{NO}_2)_2]\text{ClO}_4$  gave an absorption at  $1320\text{ cm}^{-1}$  which was more intense than its  $1390\text{ cm}^{-1}$  absorption. The  $1320\text{ cm}^{-1}$  IR spectra absorption of  $\text{Na}_3\text{Co}(\text{NO}_2)_6$ , where nitrites are cis-, was nearly equivalent to its  $1410\text{ cm}^{-1}$  absorption. The cis- isomer complex thus resulted from both methods before the chromatography, as indicated by the IR spectra.

The If trans- band fraction of the new  $[\text{Co(III)}(\text{N,N'-EtIpn})_2(\text{NO}_2)_2]^+$  complex had an orange/yellow color characteristic of analogous dinitro complexes, and its CD spectra closely resembled the CD spectra of the resolved isomers of the known trans- $[\text{Co(III)}(\text{N,N'-Melpn})_2(\text{NO}_2)_2]^+$  of Tiethof. (2) (The CD spectra of the other resolved complexes also resembled the If and trans- $[\text{Co(III)}(\text{N,N'-Melpn})_2(\text{NO}_2)_2]^+$  CD spectra. The CD spectra of the unresolved  $[\text{Co(III)}(\text{N,N'-EtIpn})(\text{NO}_2)_2]\text{-NO}_3$  resembled these CD spectra in this region also.)

The CD spectra results are tabulated in Table 2.

Table 2

$[\text{Co(III)}(\text{N,N}'\text{-Et1pn})_2(\text{NO}_2)_2]^+ \text{ A}_{1g} \rightarrow \text{T}_{1g}(\text{O}_h) \text{ CD Spectra}$

Isomer	Solvent	$\lambda_{\text{max}}, \text{cm}^{-1}$	$\Delta\epsilon$
If <u>trans,cis-</u> $[\text{Co(III)}(\text{N,N}'\text{-Et1pn})_2(\text{NO}_2)_2]^+$	Water	21,500	-3.3
If <u>trans,cis-</u> $[\text{Co(III)}(\text{N,N}'\text{-Et1pn})_2(\text{NO}_2)_2]^+$	Methanol	22,000	-3.7
<u>trans-</u> $[\text{Co(III)}(\text{N,N}'\text{-Et1pn})_2(\text{NO}_2)_2]\text{ClO}_4$	1N $\text{NaClO}_4(\text{aq})$	19,700	-
If+IIf <u>trans,cis-</u> $[\text{Co(III)}(\text{N,N}'\text{-Et1pn})_2(\text{NO}_2)_2]^+$ (rechromatographed)	2N $\text{NaClO}_4(\text{aq})$	19,000	-
$[\text{Co(III)}(\text{N,N}'\text{-Et1pn})_2(\text{NO}_2)_2]\text{NO}_3$	Water	21,600	-1.1
$[\text{Co(III)}(\text{N,N}'\text{-Et1pn})_2(\text{NO}_2)_2]\text{NO}_3$	Methanol	21,900	-1.1

The values of  $\Delta\epsilon$  (the molar ellipticity) for each If CD spectra were calculated based on the elemental analysis. The values of  $\Delta\epsilon$  for each nitrate counterion CD spectra were calculated based on weight of the sample assuming that  $[\text{Co(III)}(\text{N,N}'\text{-Et1pn})_2(\text{NO}_2)_2]\text{NO}_3\%$  was less than 100%.

At best, the  $\Delta\epsilon$  (molar ellipticity) values reported in this work for the If trans,cis- isomer of the complexes of trans-[Co(III)(N,N'-Et1pn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> were estimated to be reliable to  $\pm 0.5$  in water and  $\pm 0.7$  in methanol. This was due to the uncertainty in the elemental analysis and the uncertainty in measurement of the direct ellipticity readout from the baseline. The uncertainty of the ellipticity readout of the If fraction complex in methanol was higher than the uncertainty of the ellipticity readout of the If fraction complex in the water solution because its direct readout was closer to the assigned baseline than the If aqueous readout was. Each readout uncertainty was high because each direct readout was close to the assigned baseline due to the low effective concentration of the trans,-cis-[Co(III)(N,N'-Et1pn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> chromophore. The signal to noise ratio was the source of the uncertainty in readouts from the baseline. The lower values for the nitrate counterion isomers presumably indicated that the complex was not precipitated free from contaminating salts. In addition, the nitrate counterion complex contained some cis- isomers. Thus, its CD spectra was not due only to the trans- isomers.

Most importantly, each CD spectra, especially the chromatographed trans-[Co(III)(N,N'-Et1pn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> complexes had the expected sign for the  $A_{1g} \rightarrow T_{1g}(O_h)$

transition. The sign of the CD spectra is indicative of the stereochemistry of the complex. The CD spectra is affected by the position of groups in sectors around the Co(III) center, including nitro groups. (14,15)

trans-[Co(III)(N,N'-Et1pn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup>  
Complexes and the Hexadecadal Rule

As discussed in the introduction, it is believed that the CD spectra and the stereochemistry of trans-[Co(III)(1,2-diamine)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> complexes is spatially related by the hexadecadal rule. The CD spectra of the trans-[Co(III)(1,2-diamine)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> complexes can be related to the positions of the nitro oxygens lying preponderantly in certain sectors which affect the observed CD spectra. (15)

The farther away from the Co(III) center a substituent lies in a hexadecadal sector, the less is its influence on the ellipticity of the CD spectra. (50) To affect the CD spectra, the substituent must be in a sector away from nodal planes. (2,15,18) Thus, for example, it is known that N-CH<sub>3</sub> groups, which are further from the N<sub>4</sub> nodal plane than chelate ring methylene or C-CH<sub>3</sub> groups, have a greater effect on the intensity of d-d absorptions in the CD spectra than have the chelate ring methylene or C-CH<sub>3</sub> groups. (2,14)

Based on x-ray studies of meridial-trinitro-

triamminecobalt(III) (51) and on x-ray studies of (+)-cis-[Co(III)(1pn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]Cl (52) the nitro group N-O bonds in the trans-[Co(III)(N,N'-Etlpn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> chromophore in this work were assumed to be 1.2-1.3 Å in length, with the Co(III)-N bonds 2 Å in length and the Co(III)-NO<sub>2</sub> bonds slightly shorter than the Co(III)-N bonds. The O-N-O angles were assumed to be 120°.

Using these values, the nitro oxygens were determined to be 1-1.8 Å from the O<sub>2</sub>N-Co(III)-NO<sub>2</sub> axis and about 2.7 Å from the Co(III)-N<sub>4</sub> plane. This was well within the N<sub>4</sub> perimeter and of a distance from the Co(III) center about 1 Å less than the distance of a N-CH<sub>3</sub> or N-Et group. Thus, the nitro oxygens should have had an appropriately large influence on the CD spectra within the hexadecadal sectors. (14,15,50) The influence of these nitro oxygens must be considered great enough to have played a part in the CD spectra of known complexes with trans-[Co(III)(1,2-diamine)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> chromophores (2,12,14,15,17) and on the complexes with the trans-[Co(III)(N,N'-Etlpn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> chromophore prepared in this work.

The greatly negative ellipticity value of -3 at 21,000 cm<sup>-1</sup> in water for the newly prepared trans-[Co(III)(N,N'-Etlpn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> complexes of this work was due in large part to the position of the nitro oxygens orienting in certain hexadecadal sectors. This

value of -3 is similar to the ellipticity value of -2.8 at  $21,600\text{ cm}^{-1}$  in water reported by Tiethof for trans, - trans-[Co(III)(N,N'-Melpn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> complexes, which would suggest that it is also due in large part to the position of the nitro oxygens orienting in certain hexadecadal sectors. (2) In addition, the observed molar ellipticity values of other trans-[Co(III)(1,2-diamine)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> complexes from other workers' reports (2,3,12,17,19) is shown in this work to be due to the position of nitro oxygens orienting in these certain sectors.

Tiethof (2) has shown that for trans-[Co(III)(N,N'-Melpn)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> isomers, in which the  $A_{1g} \rightarrow A_{2g}$  and  $A_{1g} \rightarrow E_g$  transitions observed in the CD spectra are far apart in energy, the absolute value of the  $A_{1g} \rightarrow E_g$  transition observed in the CD spectra is significantly more than the value of the  $A_{1g} \rightarrow A_{2g}$  transition observed in the CD spectra. The  $A_{1g} \rightarrow E_g$  transition observed in the CD spectra is of opposite sign to the  $A_{1g} \rightarrow A_{2g}$  transition observed in the CD spectra. For the trans-[Co(III)N<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup> complexes with  $\lambda$ -chelate ring ligands, the sign of the  $A_{1g} \rightarrow A_{2g}$  transition observed in the CD spectra is positive while the sign of the  $A_{1g} \rightarrow E_g$  transition observed in the CD spectra is negative. Tiethof (2) also showed that the expected individual contribution to CD spectra for the

$A_{1g} \rightarrow E_g$  transition was approximately negative seven times the contribution to the CD spectra for the  $A_{1g} \rightarrow A_{2g}$  transition.

In the CD spectra of the trans-[Co(III)(1,2-diamine) $_2$ (NO $_2$ ) $_2$ ] $^+$  complexes, the  $A_{1g} \rightarrow A_{2g}$  and  $A_{1g} \rightarrow E_g$  transitions overlap to give one  $A_{1g} \rightarrow T_{1g}(O_h)$  band. (2,17) It is assumed that in trans-[Co(III)(1,2-diamine) $_2$ (NO $_2$ ) $_2$ ] $^+$  complexes, the relative intensity of these components, as well as their sign, remains generally constant. The  $A_{1g} \rightarrow E_g$  transition is dominant and quenches the smaller intensity of the oppositely signed  $A_{1g} \rightarrow A_{2g}$  transition observed in the CD spectra. (17) Thus, the sign of the one broad  $A_{1g} \rightarrow T_{1g}(O_h)$  band in the trans-[Co(III)(N,N'-Et1pn) $_2$ (NO $_2$ ) $_2$ ] $^+$  complexes was the net result of substituents which primarily affect the  $A_{1g} \rightarrow E_g$  transition observed in the CD spectra. The signs of the  $A_{1g} \rightarrow E_g$  transitions observed in the CD spectra which are induced by substituents in the hexadecadal sectors in the +z direction for the trans-[Co(III)(N,N'-Et1pn) $_2$ X $_2$ ] $^+$  chromophore are illustrated in Figure 8.



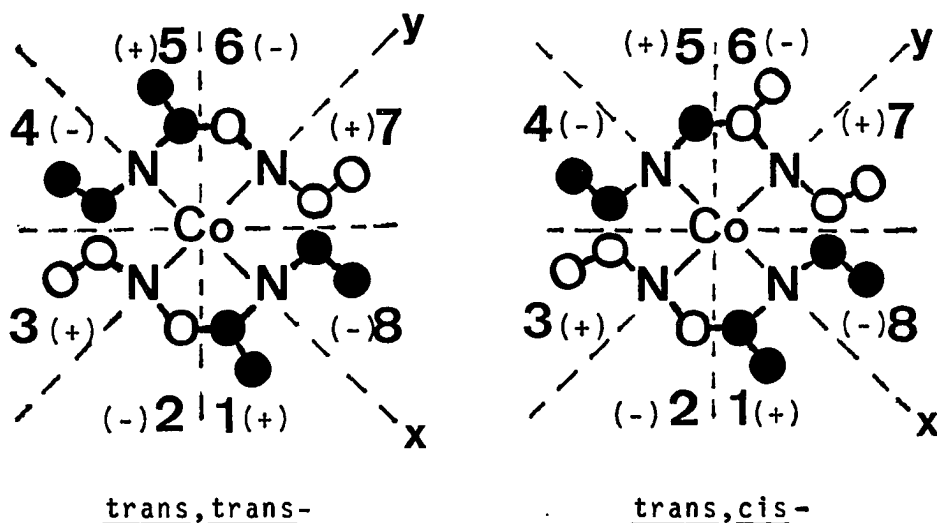


Figure 8. Signs of Hexadecadal Rule Sectors for  $A_{1g} \rightarrow E_g$  CD Transitions with trans-[Co(III)(N,N'-Etlpn) $_2$ -X $_2$ ] $^+$  Isomers. Hexadecadal rule sectors have been numbered as from Figure 3 of this work. The signs in parenthesis are for the  $A_{1g} \rightarrow E_g$  transition in the +z direction (toward reader). The signs in the -z direction are opposite. Carbon atoms in the +z direction to the Co(III)N $_4$  plane are represented by solid circles (●) and in the -z direction by open circles (○). The trans,trans- isomer is on the left. The trans,cis- isomer is on the right.

For the structurally analogous trans-[Co(III)-(N,N'-Melpn) $_2$ X $_2$ ] $^+$  chromophore, Tiethof (2) has shown that when X was Cl $^-$ , the  $A_{1g} \rightarrow A_{2g}$  transition molar ellipticity was +1.59 for the trans,trans- isomer and +1.62 for the trans,cis- isomer. The  $A_{1g} \rightarrow E_g$  transition molar ellipticity was -2.42 for the known trans,trans- isomer of the [Co(III)(N,N'-Melpn) $_2$ Cl $_2$ ] $^+$  complex and -2.37 for the trans,cis- isomer. (2) To two significant figures, the net  $A_{1g} \rightarrow A_{2g}$  transition plus

$A_{1g} \rightarrow E_g$  transition molar ellipticity for the trans- $[\text{Co(III)(N,N'-Melpn)}_2\text{Cl}_2]^+$  chromophore is  $1.6 - 2.4 = -0.8$ . However, when X was  $\text{NO}_2^-$  the net  $A_{1g} \rightarrow T_{1g}(O_h)$  transition molar ellipticity for the trans,trans- isomer of  $[\text{Co(III)(N,N'-Melpn)}_2\text{X}_2]^+$  was reported to be from -2.75 to -2.77. (2) To two significant figures, this  $A_{1g} \rightarrow T_{1g}(O_h)$  transition molar ellipticity for trans- $[\text{Co(III)(N,N'-Melpn)(NO}_2)_2]^+$ , assumed in this work to result from the molar ellipticity of the  $A_{1g} \rightarrow A_{2g}$  plus  $A_{1g} \rightarrow E_g$  transitions, is of an intensity -2.0 beyond the expected net result, which does not consider the four nitro oxygens' contribution to the net CD spectra. Likewise, the  $A_{1g} \rightarrow T_{1g}(O_h)$  transition molar ellipticity for the known  $(-)_D$ -trans- $[\text{Co(III)(N,N'-Meen)}_2(\text{NO}_2)_2]^+$  complex (2) is of an intensity -2.0 beyond the expected net result if the contributions from the nitro oxygens are similarly not considered. The case of the trans- $[\text{Co(III)(N,N'-Etlpn)}_2(\text{NO}_2)_2]^+$  complexes prepared in this work was assumed to be similar to this.

The nitro oxygens must have been preponderantly oriented in sectors which have a negative effect on the dominant  $A_{1g} \rightarrow E_g$  transition observed in the CD spectra to result in the ellipticity of -3 for trans- $[\text{Co(III)(N,N'-Etlpn)}_2(\text{NO}_2)_2]^+$  in this work, and -2.8 for trans- $[\text{Co(III)(N,N'-Melpn)}_2(\text{NO}_2)_2]^+$  in the work of Tiethof. (2) Thus, the nitro oxygens must have been in the +2

and +6, +4 and +8, -1 and -5, or -3 and -7 sectors.

More exactly, the position of the nitro oxygens for both the trans,trans- and trans,cis- isomers of trans- $[\text{Co(III)}(\text{N,N}'\text{-Et1pn})_2(\text{NO}_2)_2]^+$  is proposed to have been preponderantly in the +2 and +6, and the -1 and -5 sectors. This is illustrated in Figure 9.

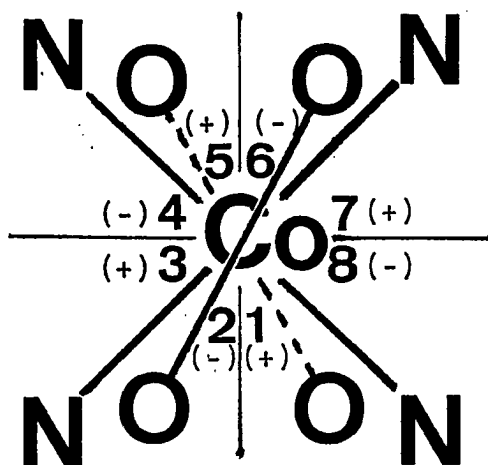


Figure 9. Proposed Position of Nitro Oxygens in trans- $[\text{Co(III)}(\text{N,N}'\text{-Et1pn})_2(\text{NO}_2)_2]^+$  Isomers. Hexadecadal sectors have been numbered as from Figure 3 of this work. The signs in parenthesis are for the A<sub>1g</sub> → E<sub>g</sub> transition observed in the CD spectra in the +z direction (toward reader). The signs in the -z direction are opposite. The dotted line are bonds to nitro oxygens below the Co(III)N<sub>4</sub> plane. Nitro nitrogens have been eliminated from the figure for clarity.

The position of the nitro oxygens in the trans- $[\text{Co(III)}(\text{N,N}'\text{-Melpn})_2(\text{NO}_2)_2]^+$  isomers and (-)<sub>D</sub>-trans- $[\text{Co(III)}(\text{N,N}'\text{-Meen})_2(\text{NO}_2)_2]^+$  complex of Tiethof (2) is proposed to have also been the same. Thus, the nitro

groups in each trans-[Co(III)(1,2-diamine)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> complex with the 1,2-diamines of N,N'-Et1pn (this work), and N,N'-Meen and N,N'-Melpn (2) were twisted from the general planes formed by the intersections of the O<sub>2</sub>N-Co-NO<sub>2</sub> axis and each of the N-C-N axes. The planes formed by each Co-NO<sub>2</sub> grouping were askew, which formed an acute angle with each other within these sectors bounded by the λ-chelate rings.

The reason these nitro oxygen positions were chosen was partly because of proposed polar intramolecular bonding, between the partially negative nitro oxygens and the partially positive (acidic) hydrogens of the λ-chelate rings. Of course, the amino hydrogens are included as partially positive hydrogens of the λ-chelate rings, and their intramolecular bonding with the nitro oxygens is generally considered hydrogen bonding. (51) The intramolecular bond distances discussed support the involvement of polar intramolecular bonding such as hydrogen bonding within the chromophore. (51) This bonding is illustrated in Figure 10.

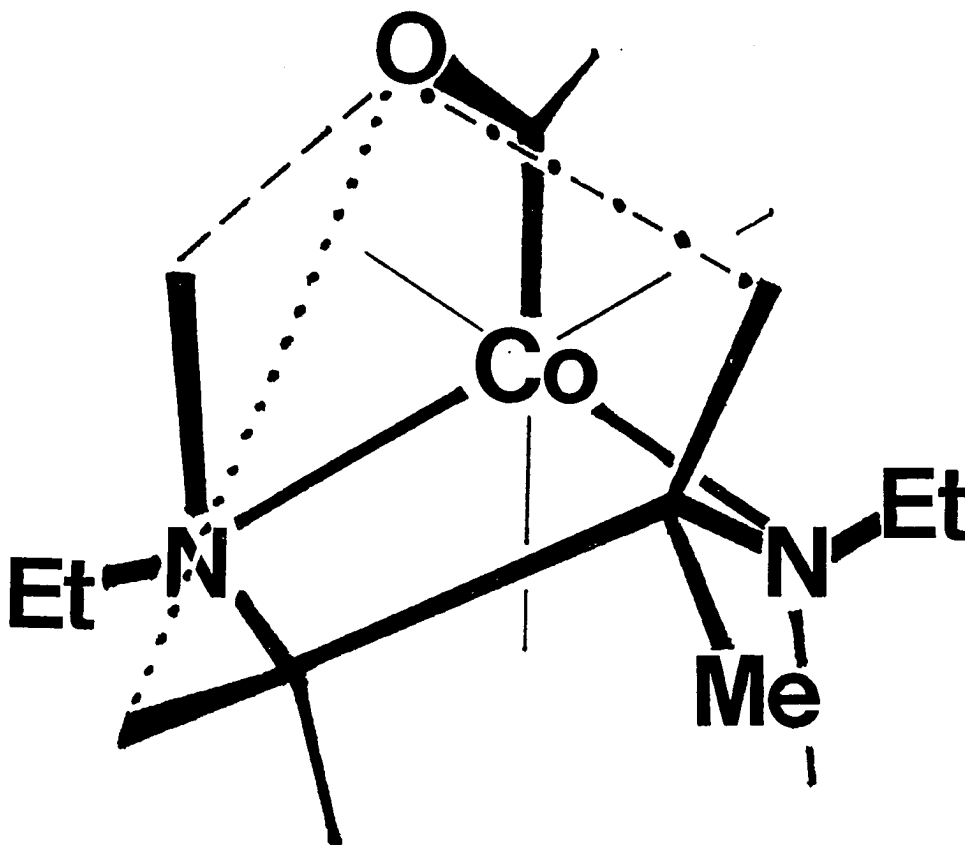


Figure 10. Intramolecular Bonding with  $\lambda$ -chelate Ring Hydrogens and Nitro Oxygens in  $\text{trans-[Co(III)(N,N'-Et1pn)}_2(\text{NO}_2)_2]^+$ . Dashed lines (---) indicate hydrogen bonding with the chelated secondary amino hydrogens. Dashed/dotted lines (-.-.-) indicate bonding with tertiary carbon hydrogens, and dotted lines (.....) indicate bonding with secondary carbon hydrogens, of the  $\lambda$ -chelate ring.

These more exact positions of the nitro oxygens in the +2 and +6, and -1 and -5 sectors were selected to be where the conformational population of the otherwise freely rotating nitro group preponderantly remained not only because of hydrogen bonding which included the secondary amino hydrogens, but also because the slightly positive (acidic) hydrogens of the  $\lambda$ -chelate ring were involved in polar intramolecular bonding with the nitro oxygens. No such hydrogen bonding system was available which would orient the nitro oxygens preponderantly in the other sectors (+4 and +8, and -3 and -7) and produce the net negative  $A_{1g} \rightarrow T_{1g}(O_h)$  transition observed in the CD spectra from influence on the dominant  $A_{1g} \rightarrow E_g$  transition. In the +4 and +8, and -3 and -7 sectors, the combination of distances between the secondary amino and chelate ring carbon hydrogens are greater and the slightly negative alternate secondary amino nitrogen (with its hydrogen in the other hemisphere) in between was not conducive to orienting the nitro oxygens in the +4 and +8, and -3 and -7 sectors.

In addition, the N-Et groups sterically hindered the positioning of the nitro oxygens in the +4 and +8, and -3 and -7 sectors. It is suggested that this steric effect in complexes such as this is substantial. (53)

The selection of these more exact positions of the nitro oxygens as previously shown in Figure 9 was

supported by the lower molar ellipticities of other known trans-[Co(III)(1,2-diamine)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> complexes that did not have all of the essential features as did both  $\lambda$ -chelate rings of the trans-[Co(III)(N,N'-Et1pn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> and the (-)<sub>D</sub>-trans-[Co(III)(N,N'-Meen)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> and trans-[Co(III)(N,N'-Melpn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> complexes. These essential features of both chelate rings were: first, two chelated secondary amines per ring; and second, an assured absolute configuration of the chelated ring.

The lower contributions from oriented nitro oxygens to the molar ellipticities of other known trans-[Co(III)(1,2-diamine)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> complexes (A-F) including complexes with both 1,2-diamines of N,N'-Meen (G), N,N'-Melpn (H) or N,N'-Et1pn (I) are tabulated in Table 3.

Table 3

Net CD Spectra Assuming Cylindrically Symmetrical  
trans-[Co(III)(1,2-diamine)]<sup>+</sup> Complexes

Complex ion	$\Delta\epsilon$ Calc	$\Delta\epsilon$ Found	Ref.	NO <sub>2</sub> <sup>-</sup> Contr.
A. <u>trans,trans</u> -[Co(III)- (N-Medpn) <sub>2</sub> (NO <sub>2</sub> ) <sub>2</sub> ] <sup>+</sup>	0.35	+0.80	(12)	1.4
B. <u>trans,trans</u> -[Co(III)- (N'-Medpn) <sub>2</sub> (NO <sub>2</sub> ) <sub>2</sub> ] <sup>+</sup>	-0.57	+0.92	(12)	1.5
C. (-) <sub>D</sub> - <u>trans,trans</u> - [Co(III)(N-Meen) <sub>2</sub> (NO <sub>2</sub> ) <sub>2</sub> ] <sup>+</sup>	-0.46	-0.70	(17)	-1.1
D. <u>trans,cis</u> -[Co(III)- (l <sub>1</sub> pn)(N,N'-Mel <sub>1</sub> pn)(NO <sub>2</sub> ) <sub>2</sub> ] <sup>+</sup>	0.40	-1.32	(2,19)	-1.8
E. <u>trans</u> -[Co(III)(en)- (N,N'-Mel <sub>1</sub> pn)(NO <sub>2</sub> ) <sub>2</sub> ] <sup>+</sup>	0.5	-1.23	(2,19)	-1.8
F. (-) <sub>D</sub> - <u>trans</u> -[Co(III)(en)- (N,N'-Meen)(NO <sub>2</sub> ) <sub>2</sub> ] <sup>+</sup>	0.46	-1.23	(2,19)	-1.7
G. (-) <sub>D</sub> - <u>trans</u> -[Co(III)- (N,N'-Meen) <sub>2</sub> (NO <sub>2</sub> ) <sub>2</sub> ] <sup>+</sup>	0.35	-1.62	(2,3)	-2.0
H. <u>trans</u> -[Co(III)- (N,N'-Mel <sub>1</sub> pn) <sub>2</sub> (NO <sub>2</sub> ) <sub>2</sub> ] <sup>+</sup>	-0.8	-2.8	(2,19)	-2.0
I. <u>trans,cis</u> -[Co(III)- (N,N'-Et <sub>1</sub> l <sub>1</sub> pn) <sub>2</sub> (NO <sub>2</sub> ) <sub>2</sub> ] <sup>+</sup>		-3.4	This Work	

The calculated (Calc) net values of  $\Delta\epsilon$  are calculated from the complexes with X = Cl<sup>-</sup> and equals  $\Delta\epsilon(A_{1g} \rightarrow A_{2g}) + \Delta\epsilon(A_{1g} \rightarrow E_g)$ . For example, the calculated net value of complex H is found from adding the  $\Delta\epsilon$  value reported for the  $A_{1g} \rightarrow A_{2g}$  transition observed in the CD spectra for trans-[Co(III)(N,N'-Mel<sub>1</sub>pn)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> ( $\Delta\epsilon(A_{1g} \rightarrow A_{2g})$ ), which is +1.6, to the reported  $\Delta\epsilon(A_{1g} \rightarrow E_g)$  value, which is -2.4. Thus, the calculated net value for complex H, assuming cylindrical symmetry about the X-Co-X axis, is -0.8. The found net values are from the complexes with X = NO<sub>2</sub><sup>-</sup>. Complexes A and B have  $\delta$ -chelate rings. Complexes C-I have  $\lambda$ -chelate rings, excepting for the non-stereospecific en ligand.



Complexes A and B show the effect of not having both the amino groups of the 1,2-diamine chelate rings be secondary amino groups. In complexes A and B the primary amino groups each have two hydrogens, one in each hemisphere of the same absolutely numbered sectors. These additional hydrogens also participate in hydrogen bonding and presumably help orient the nitro oxygens more of the time over sectors which have negative sign effects on the dominant  $A_{1g} \rightarrow E_g$  transition and nodal planes which divide sectors, more of the time. Thus, the maximum suggested positive value of 2.0 which may be contributed from the nitro groups in these  $\delta$ -chelate ring complexes was diminished by the hydrogen bonding of the primary amino group hydrogens. (Remember that complexes A and B have  $\delta$ -chelate rings and are mirror image complexes to complexes with  $\lambda$ -chelate rings. Thus, the effect of the hydrogen bonding of the primary amino group hydrogens diminished the net positive sign effect expected in these  $\delta$ -chelate ring complexes.) In that way the nitro oxygens are not preponderantly oriented in sectors which have only positive sign effects on the dominant  $A_{1g} \rightarrow E_g$  transition observed in the CD spectra and do not contribute as much to the CD spectra. The net contribution of two added N-methyl groups would have only been  $2(0.44-0.38) = 0.12$ , (2,19) which when added to the values of 0.80 and 0.92 shows that the effect of

not having both amino groups of the 1,2-diamine chelate ring secondary amino groups is itself large.

Complex C lacks each of the essential features. In addition to not having both amino groups of the 1,2-diamine chelate ring secondary, it has the least assured absolute ring configuration in comparison to complexes A and B. (1,12,54) A changing absolute ring configuration would alter the vectors of the polar attractions with the nitro oxygens. This changing absolute ring configuration is not to be confused with changing general ring configuration such as in resonance from  $\lambda$ - to  $\delta$ -chelate rings, for example. The PMR spectra of complex C does not converge into one peak, but remains split, (17) which shows that the general ring configuration of the complex remains intact. (55) Changing absolute ring configuration refers to changes on the order of vibrations, which may tend to "flatten" a ring somewhat without changes such as from  $\lambda$  to  $\delta$ -chelate rings. However, this effect of changing absolute ring configuration in complex C was assumed minimal in comparison with essential chelate ring feature of two chelated secondary amines per ring.

Complex D contains one chelate ring (involving the lpn) that does not have any secondary amino hydrogens. Instead, the  $\lambda$ -chelate ring with lpn contains four amine hydrogens from the primary 1,2-diamine. Thus, complex D

shows an effect on the CD spectra similar to complexes A and B, where the primary amino hydrogens help orient the nitro oxygens over sectors which have positive sign effects on the dominant  $A_{1g} \rightarrow E_g$  transition.

Complexes E and F each contain one chelate ring that does not have any secondary amino hydrogens. Thus, the complexes E and F have their CD spectra affected in a manner to complex D. In addition, complexes E and F each have one chelate ring (involving the en) that has a changing general ring configuration, which does indeed change from the  $\lambda$ - to the  $\delta$ -configuration. (1) This contributes to the inability of complexes E and F to orient the nitro oxygens as effectively as the other complexes.

Molecular models also supported the assignment in this work of the nitro oxygens to the +2 and +6, and -1 and -5 sectors, especially in the complexes of trans- $[\text{Co(III)}(\text{N,N'-Melpn})_2(\text{NO}_2)_2]^+$  and  $(-)_D$ -trans- $[\text{Co(III)}-(\text{N,N'-Meen})_2(\text{NO}_2)_2]^+$  and most especially trans- $[\text{Co(III)}-(\text{N,N'-Etlpn})_2(\text{NO}_2)_2]^+$ . In these sectors there was no steric interference from the N,N'-methyl or N,N'-ethyl groups such as found in the +4 and +8 and -3 and -7 sectors in these complexes (G, H and I). (53)

Solvent Dependence on the CD Spectra  
of  $\text{trans-[Co(III)(N,N'-Et1pn)}_2(\text{NO}_2)_2]^+$

The entire  $A_{1g} \rightarrow T_{1g}(O_h)$  band of  $\text{trans-[Co(III)-(N,N'-Et1pn)}_2(\text{NO}_2)_2]^+$  in the CD spectra shifted to lower wavenumbers as the solvent became more polar. The progressive shift was observed when the solvent was changed from methanol to water to 1 M  $\text{NaClO}_4(\text{aq})$  to 2 M  $\text{NaClO}_4(\text{aq})$ . Such a CD spectra change to lower energy with increased polarity of the solvents has been observed for  $\text{trans-[Co(III)(1pn)}_2\text{Cl}_2]^+$  and  $\text{trans-[Co(III)(1pn)}_2\text{Br}_2]^+$  (37) but not to the extent observed with the  $\text{trans-[Co(III)(N,N'-Et1pn)}_2(\text{NO}_2)_2]^+$  complexes of this work. The formation of solvated species with the chromophore that affected the transition energies and ellipticities which can be recorded by CD spectra resulted from the ability of a solvent medium to form stronger hydrogen bonds with the chromophore. (37) The  $\text{trans-[Co(III)-(N,N'-Et1pn)}_2(\text{NO}_2)_2]^+$  chromophore not only had positive hydrogens but had negative nitro oxygens which are capable of hydrogen bonding with the solvent. Thus, the effect on the CD spectra was large.

$\text{trans-[Co(III)(NH}_3)_2(1,2\text{-diamine)}X_2]X$  Complexes

The complex  $\text{trans-[Co(III)(NH}_3)_2(1\text{pn)Br}_2]\text{Br}$  was prepared by the method of Saburi, Tsujito & Yoshikawa.

(12) The yields were higher than the yield Hawkins, Larsen & Olsen reported by first precipitating the perchlorate salt and then converting it to the bromide salt by 63% HBr. (13) It is somewhat surprising that Hawkins, Larsen & Olsen (13) did not use this more direct method because they prepared the  $\text{NH}_4[\text{Co(III)}-(\text{NH}_3)_2(\text{lpn})(\text{SO}_3)_2]$  intermediate by the method of Bailar & Peppard. (30) Bailar & Peppard (30) had reported that a direct method to trans- $[\text{Co(III)}(\text{NH}_3)_2(\text{en})\text{Br}_2]\text{Br}$  from the reaction of  $\text{NH}_4[\text{Co(III)}(\text{NH}_3)_2(\text{en})(\text{SO}_3)_2]$  and HBr was successful. This direct method was similar to the method of Saburi, Tsujito & Yoshikawa. (12)

Similarly, the new complex trans- $[\text{Co(III)}(\text{NH}_3)_2-(\text{lpn})\text{Cl}_2]\text{Cl}$  was prepared. The new complex was separated by a method similar to the chromatography method reported by LeMay & Aalbers. (32) Hawkins, Larsen & Olsen (13) reported they could not obtain any crystals of trans- $[\text{Co(III)}(\text{NH}_3)_2(\text{lpn})\text{Cl}_2]\text{Cl}$  by a method similar to that used to prepare the corresponding dibromo complex in their work. They prepared trans- $[\text{Co(III)}-(\text{NH}_3)_2(\text{lpn})\text{Cl}_2]\text{HSO}_4$  by a lengthy method from the corresponding dibromo complex. The complex trans- $[\text{Co(III)}-(\text{NH}_3)_2(\text{lpn})\text{Cl}_2]\text{ClO}_4$  had also been reported. (15) The major contaminant in the non-optimized preparation of trans- $[\text{Co(III)}(\text{NH}_3)_2(\text{lpn})\text{Cl}_2]\text{Cl}$  in this work was assumed

to be the tetraammine complex, based on the elemental analysis. Conversion to the cis-Cl<sub>2</sub> complex was readily accomplished. (12)

The other trans-[Co(III)(NH<sub>3</sub>)<sub>2</sub>(1,2-diamine)X<sub>2</sub>]X complexes were not separated, except for trans-[Co(III)-(NH<sub>3</sub>)<sub>2</sub>(N,N'-Meen)Cl<sub>2</sub>]Cl. Each attempted preparation was from HBr or HCl reaction with the corresponding NH<sub>4</sub>[Co(III)(NH<sub>3</sub>)<sub>2</sub>(1,2-diamine)(SO<sub>3</sub>)<sub>2</sub>].

The CD Spectra of the trans-[Co(III)(NH<sub>3</sub>)<sub>2</sub>(1pn)X<sub>2</sub>]X Complexes

The absolute value of the molar ellipticity of the A<sub>1g</sub> → E<sub>g</sub> transition of trans-[Co(III)(NH<sub>3</sub>)<sub>2</sub>(1pn)Br<sub>2</sub>]Br was greater in ethanol than in methanol. Ethanol is a larger molecule than methanol. It is suggested that ethanol formed hydrogen bonds with the chromophore and formed a solvent layer with the chromophore which caused the greater absolute value of the molar ellipticity in the CD spectra than observed with methanol. Similar solvent effects in the CD spectra for these reasons have been noted for trans-[Co(III)(1pn)<sub>2</sub>Br<sub>2</sub>]Br with methanol and other polar solvents. (37) However, with no carbon backbone between the cis-(NH<sub>3</sub>)<sub>2</sub> groups, the ethanol involved in hydrogen bonding with the trans-[Co(III)-(NH<sub>3</sub>)<sub>2</sub>(1pn)Br<sub>2</sub>]Br complex presumably oriented in relationship to the Co(III) center of the sectors in a

manner in which the ethanol molecule could reside in sectors which had a larger negative effect on the  $A_{1g} \rightarrow E_g$  transition observed in the CD spectra here, thus providing the observed lower ellipticity. (50) These sectors are again the +2, +4, +6, +8, -1, -3, -5, and -7 sectors.

The CD spectra of the trans-[Co(III)(NH<sub>3</sub>)<sub>2</sub>(l<sub>pn</sub>)Cl<sub>2</sub>]<sup>+</sup> complex in methanol resembled the CD spectra of the trans-[Co(III)(l<sub>pn</sub>)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> complex and the CD spectra of the known trans-[Co(III)(NH<sub>3</sub>)<sub>2</sub>(l<sub>pn</sub>)Cl<sub>2</sub>]<sup>+</sup> complexes with HSO<sub>4</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup> counterions. (13,15) The molar ellipticity of the CD spectra of trans-[Co(III)(NH<sub>3</sub>)<sub>2</sub>(l<sub>pn</sub>)Cl<sub>2</sub>]<sup>+</sup>Cl<sup>-</sup> was roughly half of the molar ellipticity of trans-[Co(III)(l<sub>pn</sub>)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>Cl<sup>-</sup>, as expected. (13)

#### Complex Preparation and Stability Evaluations

The series of cobalt(III) complex preparations which were undertaken showed that the success in synthesis and the stability of the trans-[Co(III)N<sub>4</sub>X<sub>2</sub>]<sup>+</sup> complexes depended on several factors. Included in these factors were: first, the type of ligand (NH<sub>3</sub>; 1,2-diamines); second, the acido group (Cl<sup>-</sup>; Br<sup>-</sup>; NO<sub>2</sub><sup>-</sup>); third, the ligand isomerism for l<sub>pn</sub>-based 1,2-diamine ligands (trans-C-methyl groups; cis-C-methyl groups); fourth, the counterion (Cl<sup>-</sup>; Br<sup>-</sup>; ClO<sub>4</sub><sup>-</sup>; NO<sub>3</sub><sup>-</sup>) involved. The relative effect of these factors is listed in Table 4.

Table 4

Relative Instability Factors in trans-[Co(III)N<sub>4</sub>X<sub>2</sub>]<sup>+</sup>  
Complexes

Factor	Relative Instability
Ligand	N,N'-Bzlpn > N,N'-Etlpn > N,N'-Eten > N,N'-Melpn > N,N'-Meen > NH <sub>3</sub> > lpn
Acido Group	Cl <sup>-</sup> > Br <sup>-</sup> > NO <sub>2</sub> <sup>-</sup>
Ligand Isomerism	<u>trans</u> -C-methyl > <u>cis</u> -C-methyl
Counterion	Cl <sup>-</sup> > Br <sup>-</sup> ; ClO <sub>4</sub> ; NO <sub>3</sub> <sup>-</sup>

The NH<sub>3</sub> and 1,2-diamine ligand was the most important instability factor. The greatest instability in the complexes was introduced when the N,N'-Bz groups were introduced on lpn as N,N'-Bzlpn. In this work, the NH<sub>4</sub>[Co(III)(NH<sub>3</sub>)<sub>2</sub>(N,N'-Bzlpn)(SO<sub>3</sub>)<sub>2</sub>] complex reacted with 48% HBr at room temperature. No other NH<sub>4</sub>[Co(III)-(NH<sub>3</sub>)<sub>2</sub>(1,2-diamine)(SO<sub>3</sub>)<sub>2</sub>] complex did this.

The next greatest instability in the complexes was introduced when the N,N'-Et groups were introduced on lpn and en. Introducing the N,N'-Et groups on lpn caused more instability than on en for two reasons: the interference from the C-methyl group of lpn and the



higher entropy factor of the lpn backbone which oriented stereospecifically on the complexes. (1) Special note is made of the difficulty encountered in preparing the trans-[Co(III)(N,N'-Et1pn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> complexes in this work. Yields after chromatography were too low to precipitate the complex even as the perchlorate salt. In each such case with the N,N'-Et ligands, yields of the dinitro complexes were lower than with the corresponding N,N'-Me ligands. For example, in this work, the yield of [Co(III)(N,N'-Eten)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]ClO<sub>4</sub> was 14% of theory by H<sub>2</sub>O<sub>2</sub> oxidation and 10% of theory by air oxidation, whereas the yield of [Co(III)(N,N'-Meen)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]ClO<sub>4</sub> by H<sub>2</sub>O<sub>2</sub> oxidation was 32% of theory. In addition, in each case molecular models show interference from adjacent ethyl groups. Furthermore, the trans-[Co(III)(N,N'-Eten)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> complexes could not be converted to the trans-dichloro complexes by hot HCl, but decomposition occurred. This is not surprising since the HCl conversion of the corresponding dinitro complexes with enantiomeric N,N'-Mepn ligands is reported to both be successful and unsuccessful. The trans-[Co(III)(N,N'-Melpn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> complex could be converted to the trans-[Co(III)(N,N'-Melpn)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> complex with hot HCl, (2,3) but the trans-[Co(III)(N,N'-Medpn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> complex could not be converted to the trans-[Co(III)(N,N'-Medpn)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> complex and recovered. (12)

In addition, the  $[\text{Co(III)}(\text{N,N'-Eten})_2(\text{NO}_2)_2]\text{Cl}$  complex could not be resolved with AgBCS using a multitude of solvents. It is reported that the complex  $[\text{Co(III)}(\text{en})_2(\text{N-isopropylen})]\text{Cl}_3$  could only be resolved after many resolving agents were tried in many solvents, including AgBCS. (50) The resolution of  $[\text{Co(III)}(\text{N,N'-Eten})_2(\text{NO}_2)_2]\text{Cl}$  remains unreported.

The N,N'-Me groups introduced the next greatest instability involving the 1,2-diamine ligands. The pure solid trans-dibromo and trans-dichloro complexes with N,N'-Melpn could not be prepared in this work by air on hydrogen peroxide oxidations. There are no reports of such a synthetic route to these trans- $[\text{Co(III)}(\text{N,N'-Melpn})_2\text{X}_2]^+$  complexes. In addition, the recovery of N,N'-Melpn was less efficient (30%) than for N,N'-Etlpn (50%). This lower recovery rate indicates that N,N'-Melpn is more tightly coordinated to the cobalt than is N,N'-Etlpn. The higher entropy factor of N,N'-Melpn and the inability of HCl conversion of its trans-dinitro complex antipode (N,N'-Medpn) to the trans-dichloro complex (12) accounted for the assigned higher order of instability of N,N'-Melpn than of N,N'-Meen.

The ammine ( $\text{NH}_3$ ) group was assigned next in the relative instability of the ligands. The combination of cis- $\text{NH}_3$  ligands and a 1,2-diamine significantly

lowered the stability of the complex and was used as an index of acido group instability also. With cis- $\text{NH}_3$ , the attachment of 1,2-diamines with N,N'-Me, N,N'-Et and N,N'-Bz groups became increasingly difficult. Although trans- $[\text{Co}(\text{III})(\text{NH}_3)_2(1,2\text{-diamine})\text{Br}_2]\text{Br}$  complexes with the 1,2-diamines of N,N'-Bzlpn; N,N'-Etlpn; N,N'-Eten; N,N'-Melpn were presumably prepared as crude products, each of these decomposed upon purification. In this work, the N,N'-Bzlpn complex decomposed most readily, then N,N'-Etlpn, and so on. This is not surprising however, as only the corresponding complexes with N-Medpn and N'-Medpn have been reported, without the report of the N,N'-Medpn complex when other bis-(N,N'-Medpn) complexes were reported. (12)

Complexes with lpn were prepared without much difficulty. Bis(lpn) complexes were more successfully prepared than the cis- $(\text{NH}_3)_2\text{lpn}$  complexes such as trans- $[\text{Co}(\text{III})(\text{NH}_3)_2(\text{lpn})\text{X}_2]\text{X}$  with X of  $\text{Br}^-$  or  $\text{Cl}^-$ , although the cis- $(\text{NH}_3)_2\text{lpn}$  complexes were successfully prepared by simple methods.

The second relative instability factor in trans- $[\text{Co}(\text{III})(\text{N}_4\text{X}_2)]^+$  complexes was the acido (X) group present. The higher yields and purity of the trans- $[\text{Co}(\text{III})(\text{NH}_3)_2(\text{lpn})\text{Br}_2]\text{Br}$  complex in comparison with the corresponding trans-dichloro complex showed that the  $\text{Cl}^-$  ion as an acido group was more unstable than the

$\text{Br}^-$  ion. In addition, the ready conversion of the trans- $[\text{Co(III)}(\text{NH}_3)_2(\text{lpn})\text{Cl}_2]\text{Cl}$  complex to the corresponding cis- $\text{Cl}_2$  complex also showed the higher instability of the  $\text{Cl}^-$  ion. Tiethof (2) has shown that the inner sphere  $\text{Cl}^-$  group is readily hydrolyzed. Other workers, including Saburi, Tsujito & Yoshikawa (12) have also reported that the  $\text{Cl}^-$  ion is unstable in inner sphere coordination. Neither trans-dichloro nor trans-dibromo complexes with  $\text{N,N'}$ -Melpn or  $\text{N,N'}$ -Eten or  $\text{N,N'}$ -Etlpn could be directly prepared by hydrogen peroxide or air oxidation. (35,36,37) The corresponding dinitro complexes were each prepared. Thus, the order of instability of the acido groups was assigned  $\text{Cl}^- > \text{Br}^- > \text{NO}_2^-$ .

The inability to convert the trans-dinitro complexes of  $[\text{Co(III)}(\text{N,N'}$ -Meen) $_2(\text{NO}_2)_2]^+$  and  $[\text{Co(III)}(\text{N,N'}$ -Eten) $_2(\text{NO}_2)_2]^+$  with  $\text{HBr}$  was not considered indicative of the instability of  $\text{Br}^-$ . Instead the larger bromide group could simply not coordinate when the bulky  $\text{N,N'}$ -Me and  $\text{N,N'}$ -Et groups were present. (12) Molecular models support this proposition. The conversion of the known complex  $[\text{Co(III)}(\text{pn})(\text{N,N'}$ -Meen) $(\text{NO}_2)_2]\text{Cl}$  into a dull green product probably involved the substitution of the chloride counterion in the acidic medium onto the cobalt. Some  $\text{Br}^-$  substitution may have also occurred because of the lesser amount of steric hinderance from

the pn in comparison with the N,N'-Alkylen ligands.

The third trans-[Co(III)N<sub>4</sub>X<sub>2</sub>]<sup>+</sup> complex instability factor was ligand isomerism for bis(lpn)-based 1,2-diamine ligands. Based on the observation in this work that trans,trans-[Co(III)(N,N'-Etlpn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]Cl decomposed more readily than trans,cis-[Co(III)(N,N'-Etlpn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]Cl, the bis(lpn)-based ligand isomer with the C-methyl groups trans- is suggested to be less stable than the bis(lpn)-based ligand isomer with the C-methyl groups cis- to each other.

The fourth complex instability factor was the counterion present. The counterion instability assignments were based on the observed decomposition of the dinitro complexes with N,N'-Etlpn and N,N'-Eten ligands in the presence of the chloride counterion. The Br<sup>-</sup>, ClO<sub>4</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> counterions, which were all larger than Cl<sup>-</sup>, did not produce the decomposition in these complexes that the Cl<sup>-</sup> counterion did. Thus, the order of instability of the counterions was assigned Cl<sup>-</sup> > Br<sup>-</sup>; ClO<sub>4</sub><sup>-</sup>; NO<sub>3</sub><sup>-</sup>.

### Storage and Handling

The cobalt complexes were stored, as usual for most laboratory solids, in stoppered bottles. They were not considered to be highly toxic. (56)

## CHAPTER V

### SUGGESTIONS FOR FUTURE WORK

The trans-[Co(III)(N,N'-Et1pn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> complexes need to be prepared in larger quantity to obtain purer samples. A CD spectra check would be in order here.

The trans-[Co(III)(N,N'-Et1pn)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> complexes cannot be prepared directly, nor can they be prepared by reaction with hot HCl. However, elution with 0.3 N HCl of the by-product band left at the origin after the resolution of trans-[Co(III)(N,N'-Et1pn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> should again produce the trans-dichloro complex. Its CD spectra can be measured in situ in the green eluent before its decomposition. The CD spectra should help determine the effect of the N,N'-Et groups in comparison with the effect of the nitro oxygens.

In addition, the trans-[Co(III)(N,N'-Et1pn)<sub>2</sub>Br<sub>2</sub>]<sup>+</sup> and trans-[Co(III)(N,N'-Melpn)<sub>2</sub>Br<sub>2</sub>]<sup>+</sup> complexes, which were not able to be prepared either directly or by reaction of the corresponding dinitro complexes with hot HBr, should be able to be similarly produced as a by-product of the dinitro complexes made from CoBr<sub>2</sub>·6H<sub>2</sub>O. A slight reduction in the amount of NaNO<sub>2</sub> initially added should increase the yields of all these by-

products. (2) The trans-dibromo complexes should not be as unstable as the trans-dichloro, once prepared. Still, a preliminary CD spectra should be done in situ in the event the trans-dibromo complexes decompose. The elution of trans-[Co(III)(pn)<sub>2</sub>Br<sub>2</sub>]Br by an analogous method to that of LeMay & Aalbers, (32) but using methanolic 0.3 N HBr, proved successful in this work, and thus the method should also separate these trans-dibromo complexes just as the trans-[Co(III)(N,N'-Et1pn)<sub>2</sub>Cl<sub>2</sub>]Cl was separated with 0.3 N HCl.

The trans-chloronitro complexes with bis(1,2-diamine) ligands of N,N'-Meen; N,N'-Melpn; and N,N'-Eten should be prepared again. Their preparation from [Co(III)(N,N'-Eten)<sub>2</sub>]ClO<sub>4</sub> was successful. Thus, trans-[Co(III)(N,N'-Et1pn)<sub>2</sub>NO<sub>2</sub>Cl]<sup>+</sup> should also be able to be prepared, but the yield would be expected to be low. Their CD spectra should also be studied using the hexadecadal rule.

The N,N'-Bz1pn ligand should be studied further with Co(III) complexes. The ligand seems to have unique properties. The attempted preparation of the trans-[Co(III)(NH<sub>3</sub>)<sub>2</sub>(N,N'-Bz1pn)Br<sub>2</sub>]<sup>+</sup> complex showed that the intermediate NH<sub>4</sub>[Co(III)(NH<sub>3</sub>)<sub>2</sub>(N,N'-Bz1pn)(SO<sub>3</sub>)<sub>2</sub>] complex reacted with HBr at room temperature. Other complexes containing the ligand should be expected to be unstable.

Mixed N,N'-alkyl and N-methyl-N'-benzyl ligands should be prepared and complexed. For example, the ligand (S)-1-methylamino-2-ethylaminopropane could be prepared through N-Medpn. (12) The N-Medpn could be reacted with benzaldehyde. The (S)-1-methylamino-2-ethylaminopropane would result by reacting that product with ethyl iodide. (26) (S)-1-Methylamino-2-benzylaminopropane would result by reducing the benzaldehyde reaction product with a hydride reducing agent such as lithium aluminum hydride. (26,27,28,29) Their characteristics in Co(III) complexes would hopefully be intermediate between the N,N'-Melpn (or N,N'-Medpn) ligands and the corresponding N,N'-Etlpn or N,N'-Bzlpn ligands. The positional isomerism with these mixed ligands in trans-dinitro complexes should be studied, to help determine the more particular characteristics of the faster decomposition of the slowly eluting  $[\text{Co(III)(N,N'-Etlpn)}_2(\text{NO}_2)_2]\text{Cl}$  bands, assigned as the trans,trans- isomer. Solvent effects on the CD spectra of these suggested trans-dinitro complexes should be studied.

Finally, the simultaneous excitation of more than one d-d transition of trans- $[\text{Co(III)(1,2-diamine)}_2\text{Cl}_2]^+$  complexes which are observed in the CD spectra should be studied on an instrument such as the Axtell instrument. The net d-d transitions observed in the CD



spectra might be simultaneously prompted to resemble the d-d transitions observed in the CD spectra of the corresponding dinitro complexes, giving a better understanding of the magnitude of the actual d-d transitions occurring in the broad  $A_{1g} \rightarrow T_{1g}(O_h)$  band which are observed in the CD spectra of the corresponding dinitro complexes.

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