



8-1971

Stereochemistry and Circular Dichroism of Trans-Diacidobisdiamine Complexes of Cobalt(III)

Jack A. Tiethof
Western Michigan University

Follow this and additional works at: <https://scholarworks.wmich.edu/dissertations>



Recommended Citation

Tiethof, Jack A., "Stereochemistry and Circular Dichroism of Trans-Diacidobisdiamine Complexes of Cobalt(III)" (1971). *Dissertations*. 3008.
<https://scholarworks.wmich.edu/dissertations/3008>

This Dissertation-Open Access is brought to you for free and open access by the Graduate College at ScholarWorks at WMU. It has been accepted for inclusion in Dissertations by an authorized administrator of ScholarWorks at WMU. For more information, please contact wmu-scholarworks@wmich.edu.



STEREOCHEMISTRY AND CIRCULAR DICHROISM
OF TRANS-DIACIDOBISDIAMINE
COMPLEXES OF COBALT(III)

by

Jack A. Tiethof

A Dissertation
Submitted to the
Faculty of the Graduate College
in partial fulfillment
of the
Degree of Doctor of Philosophy

Western Michigan University
Kalamazoo, Michigan
August, 1971

ACKNOWLEDGMENTS

I am deeply indebted to my research advisor, Dr. D.W. Cooke. His willingness to discuss problems and other aspects of the project were always appreciated. His willingness to allow the project to be developed with much flexibility had a great deal to do with the scope and success of the work. My appreciation is also extended to Dr. R. Steinhaus of the Department of Chemistry and to Dr. G. Slomp of the Upjohn Company for stimulating and helpful discussions. The use of facilities at the Upjohn Company is acknowledged as is the financial support from a NDEA fellowship.

Jack A. Tiethof

72-6519

TIETHOF, Jack Alan, 1943-
STEREOCHEMISTRY AND CIRCULAR DICHROISM OF
TRANS-DIACIDOBISDIAMINE COMPLEXES OF COBALT(III).

Western Michigan University, Ph.D., 1971
Chemistry, inorganic

University Microfilms, A XEROX Company, Ann Arbor, Michigan

To
my wife, Ursula
and
son, Alexander

PLEASE NOTE:

**Some Pages have indistinct
print. Filmed as received.**

UNIVERSITY MICROFILMS

TABLE OF CONTENTS

	Page
LIST OF ABBREVIATIONS	viii
LIST OF TABLES	x
LIST OF FIGURES	xi
I. INTRODUCTION	1
II. STATEMENT OF PROBLEM	10
III. STEREOCHEMISTRY OF THE DIAMINES AND THEIR CHELATE RINGS	11
IV. EXPERIMENTAL	14
A. Materials	14
B. Preparation of Diamines	14
1. (R)-propylenediamine	14
2. (S)-propylenediamine	15
3. (R)-Diethyl-propylenebis(carbamate)	15
4. (R)-N,N'-dimethylpropylenediamine	16
C. Preparation of Complexes	18
1. <u>trans</u> -Dinitrobis(N,N'-dimethylethylenediamine) cobalt(III) Perchlorate, <u>trans</u> - [Co(sdmen) ₂ (NO ₂) ₂]ClO ₄	18
2. Resolution of <u>trans</u> -[Co(sdmen) ₂ (NO ₂) ₂]ClO ₄	19
3. (-) _D - <u>trans</u> -[Co(sdmen) ₂ (NO ₂) ₂]ClO ₄	19
4. (+) _D - <u>trans</u> -Dichlorobis(N,N'-dimethylethylene- diamine)cobalt(III)Chloride Hydrochloride Dihydrate, (+) _D - <u>trans</u> -[Co(sdmen) ₂ Cl ₂] Cl·HCl·2H ₂ O	20

	Page
5. Conversion of $(+)_D$ - <u>trans</u> - $[\text{Co}(\text{sdmen})_2\text{Cl}_3]^+$ to $(-)_D$ - <u>trans</u> - $[\text{Co}(\text{sdmen})_2(\text{NO}_2)_2]^+$	20
6. <u>trans</u> -Dinitroethylenediamine(N,N'-dimethylethylenediamine)cobalt(III) Perchlorate, <u>trans</u> - $[\text{Co}(\text{en})(\text{sdmen})(\text{NO}_2)_2]\text{ClO}_4$	21
7. Resolution of <u>trans</u> - $[\text{Co}(\text{en})(\text{sdmen})(\text{NO}_2)_2]\text{ClO}_4$	23
8. $(-)_D$ - <u>trans</u> - $[\text{Co}(\text{en})(\text{sdmen})(\text{NO}_2)_2]\text{ClO}_4$	24
9. Inactive <u>trans</u> -Dichloroethylenediamine(N,N'-dimethylethylenediamine)cobalt(III) Perchlorate Hemihydrate, <u>trans</u> - $[\text{Co}(\text{en})(\text{sdmen})\text{Cl}_2]\text{ClO}_4 \cdot 0.5 \text{ H}_2\text{O}$	24
10. $(+)_D$ - <u>trans</u> -Dichloroethylenediamine(N,N'-dimethylethylenediamine)cobalt(III) Perchlorate, $(+)_D$ - <u>trans</u> - $[\text{Co}(\text{en})(\text{sdmen})\text{Cl}_2]\text{ClO}_4$	25
11. Conversion of $(+)_D$ - <u>trans</u> - $[\text{Co}(\text{en})(\text{sdmen})\text{Cl}_2]^+$ to $(-)_D$ - <u>trans</u> - $[\text{Co}(\text{en})(\text{sdmen})(\text{NO}_2)_2]^+$	25
12. <u>trans</u> -Dinitrobis((R)-NN -dimethylpropylenediamine)cobalt(III) Perchlorate, <u>trans</u> - $[\text{Co}(\text{R-sdmpn})_2(\text{NO}_2)_2]\text{ClO}_4$	25
13. <u>trans</u> -Dichlorobis((R)-N,N'-dimethylpropylenediamine)cobalt(III) Perchlorate, <u>trans</u> - $[\text{Co}(\text{R-sdmpn})_2\text{Cl}_2]\text{ClO}_4$	27
14. <u>trans</u> -Dinitroethylenediamine((R)-N,N'-dimethylpropylenediamine)cobalt(III) Perchlorate, <u>trans</u> - $[\text{Co}(\text{en})(\text{R-sdmpn})(\text{NO}_2)_2]\text{ClO}_4$	28
15. <u>trans</u> -Dichloroethylenediamine((R)-N,N'-dimethylpropylenediamine)cobalt(III) Perchlorate, <u>trans</u> - $[\text{Co}(\text{en})(\text{R-sdmpn})\text{Cl}_2]\text{ClO}_4$	29
16. <u>trans</u> -Dinitro((R)-propylenediamine)((R)-N,N'-dimethylpropylenediamine)cobalt(III) Perchlorate, <u>trans</u> - $[\text{Co}(\text{R-pn})(\text{R-sdmpn})(\text{NO}_2)_2]\text{ClO}_4$	29
17. <u>trans</u> -Dichloro((R)-propylenediamine)((R)-N,N'-dimethylpropylenediamine)cobalt(III) Perchlorate, <u>trans</u> - $[\text{Co}(\text{R-pn})(\text{R-sdmpn})\text{Cl}_2]\text{ClO}_4$	32

	Page
18. <u>trans</u> -Dinitro((S)-propylenediamine)((R)-N,N'-dimethylpropylenediamine)cobalt(III) Chloride, <u>trans</u> -[Co(S-pn)(R-sdmpn)(NO ₂) ₂]Cl	32
E. Thin-layer Chromatography	35
F. Electronic Adsorption Spectra	35
G. Optical Rotations	36
H. Circular Dichroism Spectra	36
I. Proton Magnetic Resonance Spectra	36
J. Analysis of the PMR Spectrum of <u>trans</u> -[Co(sdmen) ₂ (NO ₂) ₂]Cl	36
K. Hydrogen Exchange Studies	37
L. Loss of Optical Activity Studies	38
M. Hydrolysis Studies	38
N. Analyses	39
V. RESULTS AND DISCUSSION	40
A. Preparations	40
B. Spectra	44
1. Circular dichroism and uv-visible spectra	44
2. Proton magnetic resonance	52
3. PMR spectral analysis	57
C. Detection of the Dinitro Complexes in Mixtures	60
D. The Stereochemistry of the Complexes of N,N'-Dimethylethylenediamine	63
1. Characterization of complexes	63
2. Conformational considerations and relative isomer stabilities	70

	Page
E. The Stereochemistry of the Complexes of R-N,N'- Dimethylpropylenediamine, R-sdmpn	71
1. Conformational considerations and the stereoselective coordination of R-sdmpn	71
2. Characterization of the complexes	76
3. Assignment of positional diastereomers	85
F. Assignment of the Absolute Configuration to the Complexes	86
G. Circular Dichroism and the Hexadecadal Rule	91
1. The dichloro complexes and the validity of the hexadecadal rule in the $A_{1g} \rightarrow A_{2g}$ CD region	93
2. The dichloro complexes and the validity of the hexadecadal rule in the $A_{1g} \rightarrow E_g$ CD region	100
3. The dinitro complexes and the validity of the hexadecadal rule	102
4. Final observations of the CD results and suggestions of a need for further work	104
H. Secondary Nitrogen Inversion Rates	105
1. General considerations	105
2. Hydrogen isotope exchange	109
3. Hydrolysis	111
4. Loss of optical activity and racemization	113
5. Nitrogen inversion rates	118
VI. Summary	120
VII. References	123
VIII. Vita	126

LIST OF ABBREVIATIONS

CD	Circular dichroism
en	Ethylenediamine
f-isomer	Fast isomer, fast moving positional diastereomer
k_{depr}	Rate constant of deprotonation
k_{deut}	Rate constant of deuterium exchange
k_{hy}	Rate constant of base hydrolysis
k_{inv}	Rate constant of nitrogen inversion
k_{prot}	Rate constant of protonation
k_{rac}	Rate constant of racemization
L-1,3,8,10Metrien	L-1,3,8,10-Tetramethyltriethylenetetramine
L-3,8Metrien	L-3,8-Dimethyltriethylenetetramine
men	N-Methylethylenediamine
N1mpn	(S)-N ₁ -Methylpropylenediamine
N2mpn	(S)-N ₂ -Methylpropylenediamine
ORD	Optical rotatory dispersion
pmr	Proton magnetic resonance
R-chxn	(R)-1,2- <u>trans</u> -Diaminocyclohexane
R-N1mpn	(R)-N ₁ -Methylpropylenediamine
R-N2mpn	(R)-N ₂ -Methylpropylenediamine
R-pn	(R)-Propylenediamine
R-sdmpn	(R)-N,N'-Dimethylpropylenediamine
sar	Sarcosinate anion
sdmen	N,N'-Dimethylethylenediamine
s-isomer	Slow isomer, slow moving positional diastereomer

S-pn (S)-Propylenediamine
tlc Thin-layer chromatography
trien Triethylenetetramine

LIST OF TABLES

Table		Page
I	Stereoisomers of $\text{trans-}[\text{Co}(\text{diamine})_2(\text{NO}_2)_2]^+$ Prepared and Identified	41
II	Electronic Absorption and Circular Dichroism Data of Complexes of sdmen	47
III	Electronic Absorption and Circular Dichroism Data of Complexes of R-sdmpn	50
IV	Assignment of Chemical Shift for PMR Spectra of Complexes of sdmen	53
V	Assignment of Chemical Shift for PMR Spectra of Complexes of R-sdmpn	54
VI	Possible Stereoisomers of $\text{trans-}[\text{Co}(\text{diamine})$ $(\text{R-sdmpn})\text{X}_2]^+$	77
VII	Calculated CD Intensities of the $A_{1g} \rightarrow A_{2g}$ (D_{4h})CD band for the Dichloro Complexes	96
VIII	Calculated CD Intensities of the $A_{1g} \rightarrow E_g$ (D_{4h})CD band for the Dichloro Complexes	101
IX	The CD Band Intensities for the Major $A_{1g} \rightarrow T_{1g}(O_h)$ Band Near $22,000 \text{ cm}^{-1}$ for the Dinitro Complexes	103
X	Rate Constants of Deuterium Exchange for $\text{trans-}[\text{Co}(\text{en})(\text{sdmen})(\text{NO}_2)_2]^+$	109
XI	Rate Constants of Hydrolysis for $(-)_D\text{-trans-}[\text{Co}(\text{en})(\text{sdmen})(\text{NO}_2)_2]^+$	113
XII	Rate Constants of Loss of Optical Activity for $(-)_D\text{-trans-}[\text{Co}(\text{en})(\text{sdmen})(\text{NO}_2)_2]^+$	117

LIST OF FIGURES

Figure		Page
1	Structures of the enantiomers of $[\text{Co}(\text{NH}_3)_4\text{men}]^{3+}$	2
2	Structures of the stereoisomers of <u>trans,trans</u> - $[\text{Co}(\text{men})_2(\text{NO}_2)_2]^+$	2
3	Proposed mechanism for racemization of active <u>trans,trans</u> - $[\text{Co}(\text{men})_2(\text{NO}_2)_2]^+$	3
4	Two possible conformations that result when S-Nlmpn coordinates to a metal ion	5
5	Regional sign arrangement for the contribution to the $A_{1g} \rightarrow A_{2g}(\text{D}_{4h})$ CD bands for dichlorotetramine cobalt(III) ions	7
6	Absolute configuration of $(-)_D$ -propylenediamine and $(-)_D$ -N,N'-dimethylpropylenediamine	11
7	Skew conformations of a chelated ethylenediamine	12
8	The absorption and CD spectra for $(-)_D$ - <u>trans</u> - $[\text{Co}(\text{sdmen})_2(\text{NO}_2)_2]^+$ and $(-)_D$ - <u>trans</u> - $[\text{Co}(\text{en})(\text{sdmen})(\text{NO}_2)_2]^+$	45
9	The absorption and CD spectra for $(+)_D$ - <u>trans</u> - $[\text{Co}(\text{sdmen})_2\text{Cl}_2]^+$ and $(+)_D$ - <u>trans</u> - $[\text{Co}(\text{en})(\text{sdmen})\text{Cl}_2]^+$	46
10	Absorption and CD spectra for <u>trans</u> - $[\text{Co}(\text{R-sdmpn})_2(\text{NO}_2)_2]^+$, <u>trans</u> - $[\text{Co}(\text{en})(\text{R-sdmpn})(\text{NO}_2)_2]^+$ and <u>trans</u> - $[\text{Co}(\text{R-pn})(\text{R-sdmpn})(\text{NO}_2)_2]^+$	48
11	Absorption and CD spectra for <u>trans</u> - $[\text{Co}(\text{R-sdmpn})_2\text{Cl}_2]^+$, <u>trans</u> - $[\text{Co}(\text{en})(\text{R-sdmpn})\text{Cl}_2]^+$ and <u>trans</u> - $[\text{Co}(\text{R-pn})(\text{R-sdmpn})\text{Cl}_2]^+$	49
12	The pmr spectrum of <u>trans</u> - $[\text{Co}(\text{sdmen})_2(\text{NO}_2)_2]^+$	56
13	The pmr spectrum of <u>trans</u> - $[\text{Co}(\text{sdmen})_2(\text{NO}_2)_2]^+$ in the methylene region	59
14	Pmr assignments of methylene protons of <u>trans</u> - $[\text{Co}(\text{sdmen})(\text{NO}_2)_2]^+$	60
15	Possible structures of <u>trans</u> - $[\text{Co}(\text{sdmen})_2\text{X}_2]^+$	65

Figure		Page
16	The structures of <u>trans</u> -[Co(en)(sdmen)X ₂] ⁺	68
17	Possible structures of coordinated R-sdmpn	72
18	Conformations of (S)-propylenediamine	73
19	Conformations of coordinated R-sdmpn	74
20	The conformations which result when Nlmpn coordinates with the unfavorable S configuration at the nitrogen center	75
21	Structures assigned to isomers found for <u>trans</u> -[Co(R-sdmpn) ₂ (NO ₂) ₂] ⁺	79
22	Stereoisomer assignments for the dinitro mixed(diamine) complexes of R-sdmpn	82
23	Conformations of isomers of <u>trans,trans</u> -[Co(men) ₂ X ₂] ⁺	84
24	The absolute configuration of R-sdmpn	87
25	Tetragonal splitting of excited states of Co(III) . . .	88
26	The regional sign arrangement above the Co-N ₄ plane of contributions by diamine moieties to the A _{1g} → A _{2g} (D _{4h}) CD bands	92
27	Possible distortion of coordinated R-sdmpn	99
28	Proposed mechanism for racemization and deuteration of active <u>trans,trans</u> -[Co(men) ₂ (NO ₂) ₂] ⁺	106
29	Plots of the logarithm of the peak height of the pmr N-methyl signal vs time for (-) _D - <u>trans</u> -[Co(en)(sdmen)(NO ₂) ₂] ⁺	110
30	Plots of the logarithm of absorbance vs time for (-) _D - <u>trans</u> -[Co(en)(sdmen)(NO ₂) ₂] ⁺	112
31	The ORD curve for (-) _D - <u>trans</u> -[Co(en)(sdmen)(NO ₂) ₂] ⁺ . .	113
32	Plots of log α vs time for (-) _D - <u>trans</u> -[Co(en)(sdmen)(NO ₂) ₂] ⁺	115
33	Nitrogen inversion followed by conformational interchange for coordinated deprotonated men	119

Figure	Page
34 Nitrogen inversion followed by conformational interchange for coordinated sdmen	119

I. INTRODUCTION

Within the past few years, Sargeson¹⁻⁴ and coworkers have prepared a series of transition metal complexes containing secondary amines. In these complexes the inertness of the coordinated secondary amine nitrogens toward inversion of configuration had been demonstrated. This observation has elicited much interest in the stereochemistry of these complexes. The complex ion, $[\text{Co}(\text{NH}_3)_4 \text{men}]^{3+}$,² has been shown to exist as a pair of enantiomers (shown in Figure 1) which have been resolved. Likewise, the $[\text{Co}(\text{NH}_3)_4 \text{sar}]^{2+}$ ion¹ and the $[\text{Pt}(\text{en})(\text{men})]^{2+}$ ion⁴ have also been resolved. In these complexes, the dissymmetry arises solely as a result of the coordinated asymmetric secondary nitrogens. For the same reason, a meso form and an enantiomeric pair of the trans,trans- $[\text{Co}(\text{men})_2(\text{NO}_2)_2]^+$ ion³ were isolated and characterized as having the structures shown in Figure 2. The meso form has the two secondary amine nitrogens with mirror image configurations whereas the enantiomers have the two nitrogen atoms with the same configuration.

Racemization of active trans,trans- $[\text{Co}(\text{men})_2(\text{NO}_2)_2]^+$ occurs by a base catalyzed process. It is believed to involve three steps as shown in Figure 3.^{3,5} First, the secondary nitrogen atom is deprotonated by hydroxide ion. Next, the deprotonated nitrogen atom is inverted to the mirror image configuration, and finally, the nitrogen atom is reprotonated. This results in the somewhat less stable meso form which readily isomerizes to the racemic form by further inversion of

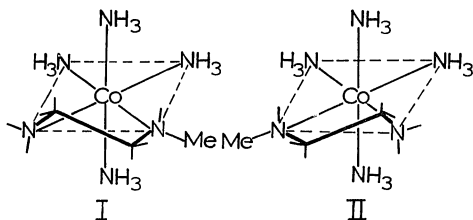


Figure 1. Structures of the enantiomers of $[\text{Co}(\text{NH}_3)_4 \text{men}]^{3+}$.

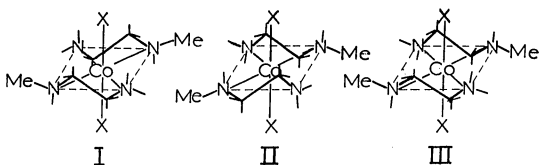


Figure 2. Structures of the stereoisomers of trans,trans-[Co(men)₂(NO₂)₂]⁺. I and II are enantiomers; III is a meso form.

one of the secondary amine nitrogen atoms. Although the ring conformer interchange has been represented as part of the inversion step in Figure 3, it is not known whether this occurs during or after the inversion step.

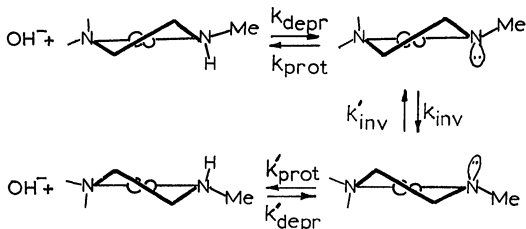


Figure 3. Proposed mechanism for racemization of active trans,trans- $[\text{Co}(\text{men})_2(\text{NO}_2)_2]^+$. Only the one men is shown.

The deuteration process of the secondary amine nitrogen atom is base catalyzed also, and obeys the same rate equation as racemization:

$$\text{rate} = k [\text{complex}] [\text{OH}^-] \quad (1)$$

Racemization and deuteration are believed to share the first step of the process in Figure 3. For deuteration, however, reprotonation occurs before inversion. The ratio of the rate constants for deuteration and racemization is about 90,000 at 34° . This reflects the fact that very few deprotonated nitrogens invert before reprotonation. This explains, then, the fact that it is possible to isolate stereoisomers which arise only because of differences in configurations

around the asymmetric nitrogen centers: these centers are very inert to inversion.

The origin of optical activity in the d-d metal transition region for complexes of amines possessing asymmetric nitrogen centers has been a point of controversy. Buckingham, *et al.*⁶ assigned the absolute configurations of $(-)_D\text{-trans,trans-}[\text{Co}(\text{men})_2\text{Cl}_2]^+$, which they prepared from the dextro dinitro complex. Their assignment was based on a comparison of the CD curve for this complex in the $A_{1g} \rightarrow T_{2g}(O_h)$ electronic transition region to those for the complex ions, $(+)_D\text{-trans-}[\text{Co}(\text{L-3,8-mtrien})\text{Cl}_2]^+$, $(+)_D\text{-trans-}[\text{Co}(\text{trien})\text{Cl}_2]^+$, $\text{trans-}[\text{Co}(\text{R-pn})_2\text{Cl}_2]^+$, and $\text{trans-}[\text{Co}(\text{R-chxn})_2\text{Cl}_2]^+$. The *gauche* (or skew) diamine side chain ring conformations in the first two complexes are known to be \int^a conformations as are the diamine rings of the later two complexes. Buckingham, *et al.* assumed that the puckering of the diamine rings was the predominant contributor to the optical activity in all of these complexes and assigned the ring conformations in $(-)_D\text{-trans,trans-}[\text{Co}(\text{men})_2\text{Cl}_2]^+$ as λ because the CD curve bears an essentially mirror image relation to those of the other *trans*-diacido-tetramine complexes which have known \int ring conformations. From conformational considerations^{2,3}, it is known that the N-methyl group in N-methyl-ethylenediamine prefers an equatorial conformation. Thus, the secondary nitrogen configurations in $(-)_D\text{-trans,trans-}$

^aThe use of \int and λ to specify the chirality of *gauche* conformations of five membered diamine chelate rings conforms with their use as specified by the Commission on the Nomenclature of Inorganic Chemistry of the International Union of Pure and Applied Chemistry.⁷ Structure I in Figure 1 is in the \int conformation whereas Structure II is λ .

$[\text{Co}(\text{men})_2\text{Cl}_2]^+$ were assigned S^b configurations.

From a study of the stereospecific coordination of N_1 -methyl-(S)-propylenediamine, Saburi, *et al.*^{9,10} concluded that Buckingham and coworkers had assigned the absolute configuration of $(-)_D$ -trans, trans- $[\text{Co}(\text{men})_2(\text{NO}_2)_2]^+$ incorrectly. When N_1 -methyl-(S)-propylenediamine coordinates to a metal ion, there are two possible gauche ring conformations (λ or δ) which the chelate ring can assume. However, X-ray^{11,12} and conformational analysis¹³⁻¹⁵ studies of complexes of $(-)_D$ -propylenediamine suggest that the C-methyl group always prefers to be in an equatorial position with respect to the metal chelate ring.

There are two possible configurations of the coordinated N-methyl nitrogen atom as shown in Figure 4. Structure I has the N-

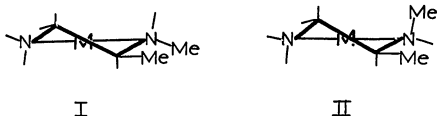


Figure 4. Two possible conformations that result when S - N_1 mpn coordinates to a metal ion. The conformations are those resulting from preferential placement of C-methyl equatorially.

^bThe use here of R and S to describe the absolute configuration about an asymmetric tetrahedral nitrogen atom conforms with the guidelines as proposed by Cahn, *et al.*⁸

methyl substituent in an equatorial position with an R nitrogen configuration while structure II has the methyl in an axial position with an S nitrogen configuration. X-ray¹⁶ and conformational analysis studies^{2,15} of complexes of N-methylethylenediamine suggest that the N-methyl prefers the equatorial orientation. Since this diamine has been shown by Saburi, et al.¹⁰ to coordinate stereospecifically, this preference must be very pronounced. In order for the N-methyl and C-methyl on the asymmetric carbon atom of known S absolute configuration to be equatorial, the ring conformation must be S and the nitrogen configuration must be R for the diamines in trans,trans- $[\text{Co}(\text{S-Nlmpn})_2\text{Cl}_2]^+$.

The CD curve for this complex is very similar to that for $(-)_\text{D}$ -trans,trans- $[\text{Co}(\text{men})_2\text{Cl}_2]^+$ in the $A_{1g} \rightarrow T_{1g}$ (Q_h) region. This resulted in Saburi and coworkers assigning a R nitrogen configuration and a δ ring conformation to the N-methylethylenediamine complex.⁹ Thus, there was a conflict with the assignment made by Buckingham and coworkers.⁶

However, this conflict was resolved shortly thereafter. The structure of $(-)_\text{D}$ -trans,trans- $[\text{Co}(\text{men})_2\text{Cl}_2]\text{ClO}_4 \cdot 0.5\text{H}_2\text{O}$ in a single crystal was determined by anomalous dispersion X-ray diffraction techniques.¹⁶ The diamine rings were found to have δ conformations and nitrogen configurations were R with the N-methyl groups in equatorial position. The assignment made by Buckingham, et al. from a CD curve comparison of this complex with other trans-dichlorotetramine complexes, which did not possess N-methyl substituents, was incorrect.

Explanations to rationalize these anomalies in the CD curves have been suggested. Hawkins¹⁷ proposed that the CD curves in the $A_{1g} \rightarrow T_{1g} (O_h)$ d-d transition region for the trans-dichlorobis(diamine)cobalt(III) complexes resulted from additive dissymmetric effects from (1) the chelate ring conformation and vicinal effects, from (2) the asymmetric carbon atoms and (3) the asymmetric secondary nitrogen atoms. In order to account for the Cotton effects discussed above, he concluded that contributions from the secondary nitrogen atoms were much larger than the other two effects combined and were of opposite sign.

Mason¹⁸ concurrently proposed a somewhat different explanation. He believed that the activity of trans-diacidotetramine complexes should in general obey a regional sign rule. He suggested that the $A_{1g} \rightarrow A_{2g}(D_{4h})$ CD band near 22,000 cm^{-1} for $(-)_D$ -trans,trans- $[\text{Co}(\text{men}_2\text{Cl}_2)]^+$, trans- $[\text{Co}(\text{R-pn})_2\text{Cl}_2]^+$ and trans,trans- $[\text{Co}(\text{s-Nlmpn})_2\text{Cl}_2]^+$ obeyed a hexadecadal rule. Applying this rule, the regions of space above and below the metal-amine plane are divided into two sets of opposite signed octants as shown in Figure 5 for $A_{1g} \rightarrow A_{2g}(D_{4h})$

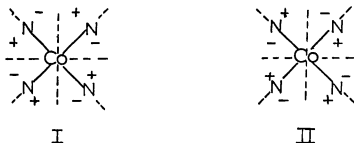


Figure 5. Regional sign arrangement for contribution to the activity of the $A_{1g} \rightarrow A_{2g}(D_{4h})$ CD bands for dichlorotetramine cobalt(III) ions (I) above the tetragonal plane and (II) below the tetragonal plane.

component band. For the above mentioned complex ions, which possess δ chelate ring conformation and R configurations at the N-methyl nitrogen atoms, the N-methyl substituents lie in negative regions whereas methylene and methylenemethylene ring moieties lie in positive sectors. In addition, it is easily seen from molecular models that the N-methyl groups lie further above the CoN_4 plane and should contribute more to the activity than to the other substituents. A hexadecadant array of opposite sign to that shown in Figure 5 describes the $A_{1g} \longrightarrow E_g$ (D_{4h}) low energy component in the $A_{1g} \longrightarrow T_{1g}$ (O_h) transition region.

This approach by Mason is a more general one than that proposed by Hawkins . Any dissymmetric trans-diacidotetramine can be described assuming the magnitude of the contributing substituents is known. For instance, it has recently been applied successfully to C-methyl and N-methyl substituted trans-diacido complexes of triethylenetetramine.

The hexadecadal rule has a theoretical basis as well. Shellman¹⁹ has treated optical activity in molecules for which the chromophore portion is not inherently dissymmetric. These molecules are treated as symmetric chromophores in which the optical activity arises because of a static dissymmetric perturbing field from the rest of the molecule. On strictly symmetry considerations, he has shown that perturbing functions must 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, to which trans-diacidotetramines can be classified in the first approximation, is the

function $XYZ(x^2-y^2)$. The regional sign dependency of this function traces out the sixteen hexadecadents in space. The bis-diamine complexes under consideration might also be looked upon as perturbed chromophores of D_{2h} symmetry. This would give rise to an octant rule. Martin, et al.²⁰ has shown that square planar complexes of tripeptides appear to obey a hexadecadal rule rather than an octant rule even though these complexes seem less related to the D_{4h} point groups than the bis-diamine complexes. Thus, based on the small amount of empirical evidence gathered to date and symmetry considerations, it appears that a hexadecadal rule should predict the activity of d-d CD bands of trans-diacidotetramine complexes.

II. STATEMENT OF PROBLEM

A series of trans-diacidobis(diamine) cobalt(III) complexes of N,N'-dimethylethylenediamine and N,N'-dimethyl-(R)-propylenediamine were prepared for the primary purpose of evaluating current theories on the origin of optical activity in dissymmetric tetragonal complexes. The dinitro complexes were prepared and characterized; the complexes of N,N'-dimethylethylenediamine were resolved into the enantiomers which arise because of the two possible configurations that the asymmetric N-methyl nitrogen atom can take. Active forms were obtained for the complexes of N,N'-dimethyl-(R)-propylenediamine from the initial complex preparation; this was because of the stereoselective coordination of the N-methyl nitrogen atom in the active diamine. In addition to these complexes, the analogous dichloro complexes were prepared directly from the active dinitro complexes. Mixed diamine complexes were also prepared with the above N-methyl substituted diamines and ethylenediamine or propylenediamine. Before their activity could be analyzed rigorously by circular dichroism, the stereochemistry of the complexes had to be ascertained. This was accomplished with generous use of proton magnetic resonance data. Finally, from deuteration and racemization data, nitrogen inversion rates were estimated for the mixed diamine complex of N,N'-dimethylethylenediamine and ethylenediamine, and the results were compared to the rates for other complexes in order to determine conformational effects on inversion rates.

III. STEREOCHEMISTRY OF THE DIAMINES AND THEIR CHELATE RINGS

The asymmetric carbon atom in $(-)_D$ -propylenediamine has been shown to exist in an R configuration as shown in Figure 6. The

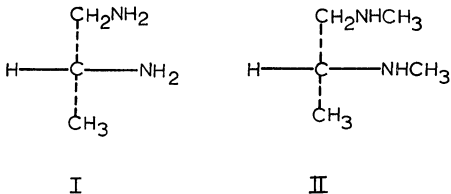


Figure 6. Absolute configuration of (I) $(-)_D$ -propylenediamine and (II) $(-)_D$,N'-dimethylpropylenediamine.

absolute configuration of this compound has been determined in two ways: it has been chemically related to D-alanine, a compound of known absolute configuration, through a conversion of the COOH in alanine to CH_2NH_2 in propylenediamine.²¹ This was confirmed when the crystal structure of a single crystal of trans-dichlorobis $(-)_D$ -propylenediamine)-cobalt(III) chloride hydrochloride dihydrate was studied by anomalous dispersion X-ray diffraction techniques.¹² The enantiomer, $(+)_D$ -propylenediamine, must have an S configuration, and in subsequent text, these enantiomers will be referred to only as (R) and (S)-propylenediamine. $(-)_D$,N'-dimethylpropylenediamine was prepared from (R)-propylenediamine by conversion of the amine

III. STEREOCHEMISTRY OF THE DIAMINES AND THEIR CHELATE RINGS

The asymmetric carbon atom in $(-)_D$ -propylenediamine has been shown to exist in an R configuration as shown in Figure 6. The

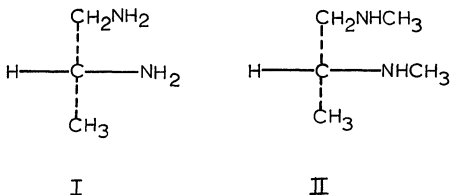


Figure 6. Absolute configuration of (I) $(-)_D$ -propylenediamine and (II) $(-)_D$ N,N'-dimethylpropylenediamine.

absolute configuration of this compound has been determined in two ways: it has been chemically related to D-alanine, a compound of known absolute configuration, through a conversion of the COOH in alanine to CH_2NH_2 in propylenediamine.²¹ This was confirmed when the crystal structure of a single crystal of trans-dichlorobis $(-)_D$ -propylenediamine)-cobalt(III) chloride hydrochloride dihydrate was studied by anomalous dispersion X-ray diffraction techniques.¹² The enantiomer, $(+)_D$ -propylenediamine, must have an S configuration, and in subsequent text, these enantiomers will be referred to only as (R) and (S)-propylenediamine. $(-)_D$ N,N'-dimethylpropylenediamine was prepared from (R)-propylenediamine by conversion of the amine

groups to methylamine groups. Thus, the configuration of the asymmetric carbon in the N-methyl derivative is also R as shown in Figure 6.

The chelate rings formed by ethylenediamine and N and C-substituted ethylenediamine are non-planar due to conformational energy requirements of the ring. Theilacker²² proposed that the ethylenediamine chelate rings take a skew conformation. Corey and Bailar¹³ were the first to do a detailed conformational analysis study of metal-ethylenediamine ring systems. They concluded that the chelate rings existed in enantiomeric skew or gauche conformations as shown in Figure 7. Hawkins,¹⁵ and Buckingham, *et al.*^{2,3} have done more

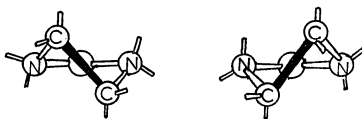


Figure 7. Skew conformations of a chelated ethylenediamine: (I) δ conformation, (II) λ conformation.

sophisticated conformational analyses of complexes of ethylenediamine and propylenediamine as well as N-methylethylenediamine. In these substituted ethylenediamine complexes, it is generally concluded that a skew conformation, which allows the methyl substituents to lie in an equatorial position, is more stable. At present there is some disagreement concerning the degree of this difference in

stability, however. This will be discussed further as it applies to this work.

IV. EXPERIMENTAL

A. Materials

All chemicals were Reagent Grade unless otherwise noted. Ethylene-diamine was 98-100% pure, and racemic propylenediamine was Practical Grade. N,N'-Dimethylethylenediamine was purchased from Ames Laboratories, Inc., Milford, Conn. The resolving agents, ammonium α -bromocamphor- η -sulfonate (NH_4BCS) and l-tartaric acid were purchased from Aldrich Chemical Co. and Mann Research Laboratories, New York, N.Y., respectively. The silver salt of the former was readily obtained using the method of Buckingham, et al.³ Deuterium oxide and deuterium chloride were purchased from Merck, Sharp and Dohm, Montreal, Quebec, and from the J.T. Baker Chemical Co. Ethyl chloroformate was Practical Grade. Tetraphenylarsonium chloride was purchased from Aldrich Chemical Co.

B. Preparation of Diamines

1. (R)-Propylenediamine

Inactive propylenediamine was resolved by ten fractional crystallizations with (+)-tartaric acid and acetic acid as described by Dwyer, et al.²³ The optically pure least soluble diastereomeric salt of (R)-propylenediamine was converted to an aqueous solution of the free amine, using the method of Bailar, et al.²⁴ ($[\alpha]_D = -33.2^\circ$ for 15 mg/ml solution in dry benzene; the value obtained by Dwyer et al. after 10 recrystallizations, $[\alpha]_D = -34.2^\circ$).

2. (S)-Propylenediamine

(S)-Propylenediamine was obtained with somewhat low optical activity using the method of Dwyer, et al.²³ ($[\alpha]_D = -31.9^\circ$ for a 8.25 mg/ml solution in dry benzene). The amine (20.7 g, 0.28 mol) was further purified by crystallization from a 10° solution, containing water (250 ml), glacial acetic acid (20 ml) and 1-tartaric acid (70.2 g, 0.56 mol) to give 92.2 g of the hydrogen 1-tartrate salt. This was recrystallized by the dissolution of the salt in boiling water (125 ml, 105 ml, 95 ml, 85 ml) followed by the addition of glacial acetic acid (7 ml) and cooling to 10°. The crystals were collected, washed with cold water (15 ml) and air dried. Four additional recrystallizations were carried out, reducing the amount of water by 10 ml and the acetic acid by 0.5 ml with each recrystallization. (Final yield: 75.3 g). The amine was found to have high optical purity ($[\alpha]_D = -33.9^\circ$ for a 21.3 mg/ml solution in dry benzene). The remaining salt was then converted to an aqueous solution of the free amine, using the method of Bailer, et al.²⁴

3. (R)-Diethyl-propylenebis(carbamate)

An aqueous solution of (R)-propylenediamine (33.8 g of 35% solution, 0.18 mol), methanol (300 ml) and sodium bicarbonate (163 g, 1.9 mol) were placed in a 1 liter flask. The mixture was cooled to 3° in an ice bath and ethylchloroformate (205 g, 1.9 mol) was added slowly through an addition funnel to the stirred mixture while the temperature was maintained at 3°-6°. After the addition was completed, the mixture was stirred for an additional 2 hours in an ice bath and

allowed to sit overnight at room temperature. The mixture was then evaporated on a rotary evaporator to a solid, which was extracted with chloroform (2-100 ml portions). The chloroform solution was evaporated to dryness on a rotary evaporator. A methanol solution (150 ml) of this solid was passed through a column (diameter, 4.2 cm) containing 300 ml of cationic exchange resin (Dowex-50-X8, 100-200 mesh) in the H^+ form at a flow rate of 2 ml/min. This was followed by additional methanol (300 ml). The total methanol solution was evaporated on a rotary evaporator to a solid, which was recrystallized from boiling ether (270 ml), cooling the solution to 6° . The solid was collected and dried under vacuum (melting point, $94.5-95.5^\circ$). Two additional fractions with similar melting points were obtained when the ether filtrates of previous fractions were evaporated to one half volume and cooled (total yield, 33.9 g, 0.16 mol). A small part of the first fraction (0.2 g) was recrystallized from boiling ether (melting point, $95-95.5^\circ$). Anal. Calcd for $C_9H_{18}N_2O_4$: C, 49.57; H, 8.27; N, 12.84. Found: C, 49.29; H, 8.16; N, 12.69.

4. (R)-N,N'-dimethylpropylenediamine

Anhydrous ether (50 ml) and lithium aluminum hydride (19 g, 0.5 mol) were placed in a dry 1 liter flask. A solution of anhydrous ether (550 ml) and (R)-diethyl-propylenebis (carbamate) (18.5 g, 0.085 mol) was added to the stirred solution through an addition funnel during a 45 min period. The resulting mixture was refluxed for 5 hr. The boiling mixture was then cooled in a water-ice bath to 10° , and sufficient water (37 g, 2.05 mol) was added dropwise

very cautiously with vigorous magnetic stirring to just quench the reaction (about 1.5 hr.). The ether and solid portions were separated by filtration and the solid portion was extracted with ether (400 ml). All of the ether fractions were combined and evaporated on a rotary evaporator at 20° to about 15 ml. This liquid was then distilled, collecting 3 fractions in the boiling range of 125.5-129° (Yield, 4.91 g, 0.048 mol).

The amine was converted to the dihydrochloride with the addition of 0.5 ml of HCl (12.4N) to an ethanol solution (5 ml) of 0.2 g of the higher boiling fraction. The solution was evaporated to an oil, which crystallized with the addition of ether (10 ml). The crystals were ground and washed in ether and dried under vacuum (yield, 0.3 g). Anal. Calcd. for $C_5H_{14}N_2 \cdot 2HCl$: C, 34.30; H, 9.22; N, 16.00. Found: C, 34.31; H, 9.22; N, 15.96. The optical rotation of the free amine was determined in a benzene solution ($[\alpha]_D = -48.5^\circ$, amine concentration, ~ 0.07 g/10 ml). The amine concentration in this benzene solution was determined by extracting the amine into water and titrating this solution with 0.1N HCl potentiometrically.

C. Preparation of Complexes

The spectral properties of all complexes prepared here are listed in the discussion (VB).

1. trans-Dinitrobis(N,N'-dimethylethylenediamine)cobalt(III) Perchlorate, trans- [Co(sdmn)₂(NO₂)₂] ClO₄

A cold solution of $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ (23.8 g, 0.1 mol, in 50 ml of H_2O) was added to a cold solution of N,N'-dimethylethylenediamine (17.6 g, 0.2 mol, in 8.1 ml of 12.4 N HCl), and NaNO_2 (15.9 g, 0.23 mol) was added quickly. The resulting solution was aerated in an ice bath for 30 min, followed by 5 hr at ambient temperature. This solution was evaporated slowly under an air stream at 25° to a paste and dried under the vacuum. The residue was ground in methanol (200 ml) and filtered, discarding the light green solid. The filtrate was evaporated to 75 ml, filtered again, and evaporated to dryness at room temperature. The residue was dissolved in 100 ml of H_2O and a NaClO_4 solution (12.2 g, 0.1 mol, in 20 ml of H_2O) was added dropwise with stirring. The desired precipitate was collected, washed with ethanol and ether, and dried under vacuum (31.8 g, 0.075 mol). Recrystallization of 1 g of this solid from 50 ml of 50% ethanol at 55° gave well developed orange crystals, although there was no change in the uv-visible absorption spectra. Anal. Calcd for $[\text{CoC}_8\text{H}_{24}\text{N}_4\text{O}_4]$ ClO_4 : C, 22.50; H, 5.67; N, 19.67. Found: C, 22.61; H, 5.52; N, 19.85.

2. Resolution of $\text{trans-}[\text{Co}(\text{sdmen})_2(\text{NO}_2)_2]\text{ClO}_4$

An aqueous solution of $\text{trans-}[\text{Co}(\text{sdmen})_2(\text{NO}_2)_2]\text{Cl}$, obtained from $\text{trans-}[\text{Co}(\text{sdmen})_2(\text{NO}_2)]\text{ClO}_4$ (7.34 g, 0.17 mol), was vigorously stirred with AgBCS (7.0 g, 0.17 mol). The mixture was filtered to remove AgCl, and the filtrate was evaporated to an oil on a rotary evaporator. 100 ml of ethanol was added and the solution was re-evaporated. The residue was dissolved in 95% ethanol (200 ml) at 50°. The volume was quickly reduced to 90 ml at 35° on a rotary evaporator. The solution was allowed to cool for 5 hr at room temperature and 2 days at 6°. The solid which formed was collected, washed with ethanol and ether, and dried under vacuum (3.0 g, 4.7 mmol, $[\alpha]_{500}^{-244^\circ}$ for 0.1% solution). Additional solid of similar activity was obtained by cooling the filtrate to -20° for several days (1.3 g). The first fraction was dissolved in 95% ethanol (160 ml at 40°), rapidly evaporated to one half volume, and cooled for 5 hrs at room temperature and then for several days at -20°. The well developed orange crystals were collected, washed with ethanol and ether, and dried under vacuum (1.7 g, $[\alpha]_{500}^{-340^\circ}$ for a 0.1% solution). Additional recrystallizations gave only slight improvement in the optical purity of $(-)_\text{D}\text{-trans-}[\text{Co}(\text{sdmen})_2(\text{NO}_2)_2]\text{BCS}$. Further recrystallizations gave no improvement ($[\alpha]_{500}^{-350^\circ}$ for 0.1% solution).

3. $(-)_\text{D}\text{-trans-}[\text{Co}(\text{sdmen})_2(\text{NO}_2)_2]\text{ClO}_4$

$(-)_\text{D}\text{-trans-}[\text{Co}(\text{sdmen})_2(\text{NO}_2)_2]\text{BCS}$ (3.3 g, 0.47 mol), was dis-

solved in about 500 ml of 95% ethanol. A solution of LiClO_4 (2.2 g in 20 ml of ethanol) was added dropwise with stirring. The resulting solid was collected, washed with ethanol and ether, and dried under vacuum (2.2 g, $[\alpha]_{500} -680^\circ$ for 0.05% solution.) Anal. Calcd for $[\text{CoC}_5\text{H}_{24}\text{N}_4\text{O}_4]\text{ClO}_4$: C, 22.50; H, 5.67; N, 19.70. Found: C, 22.42; H, 5.63; N, 19.86.

4. $(+)\text{-D-trans-Dichlorobis}(N,N'\text{-dimethylethylenediamine})\text{cobalt(III)}$
Chloride Hydrochloride Dihydrate, $(+)\text{-D-trans-}[\text{Co}(\text{sdmen})_2\text{Cl}_2]$
 $\text{Cl}\cdot\text{HCl}\cdot 2\text{H}_2\text{O}$

An aqueous solution of $(-)\text{-D-trans-}[\text{Co}(\text{sdmen})_2(\text{NO}_2)_2]\text{ClO}_4$ (0.75 g, 1.15 mmol) was mixed with tetraphenylarsonium chloride (0.6 g, 1.4 mmol) removing most of the ClO_4 as a precipitate. The solution was evaporated on a rotary evaporator to a solid. This was dissolved in HCl (17 ml of 12.4 N) and heated on a steam bath for 1 hr at $65\text{-}70^\circ$. Upon cooling at room temperature, large dark green crystals formed. They were collected, washed with cold 6N HCl , ethanol and ether, and dried under vacuum ($[\alpha]_{\text{D}} + 890^\circ$ for 0.075% solution). Anal. Calcd for $[\text{CoC}_5\text{H}_{24}\text{N}_2\text{Cl}_2]\text{Cl}\cdot\text{HCl}\cdot 2\text{H}_2\text{O}$: C, 23.29; H, 7.05; Cl, 34.26; N, 13.60. Found: C, 22.97; H, 7.28; Cl, 33.95; N, 13.76. Inactive $\text{trans-}[\text{Co}(\text{sdmen})_2\text{Cl}_2]\text{Cl}\cdot\text{HCl}\cdot 2\text{H}_2\text{O}$ was prepared in a manner similar to the active form.

5. Conversion of $(+)\text{-D-trans-}[\text{Co}(\text{sdmen})_2\text{Cl}_2]^+$ to $(-)\text{-D-trans-}[\text{Co}(\text{sdmen})_2(\text{NO}_2)_2]^+$

A solution (25 ml) of $(+)\text{-D-trans-}[\text{Co}(\text{sdmen})_2\text{Cl}_2]\text{Cl}\cdot\text{HCl}\cdot 2\text{H}_2\text{O}$

(0.1%, 0.06 mmol) and NaNO_2 (1.25 g, 20 mmol) in 0.01 N HClO_4 was prepared, and the change in rotation at 500 nm was followed while the solution was maintained at room temperature. After 2 days, the rotation ceased to change and the absorption spectrum in the 400 nm-600 nm region was indistinguishable from that for a similar solution of $(-)_D\text{-trans-}[\text{Co}(\text{sdmen})_2(\text{NO}_2)_2] \text{ClO}_4$. The rotation in a 0.5 cm cell had changed from $+0.21^\circ$ to -0.29° during that time.

6. trans-Dinitroethylenediamine(N,N -dimethylethylenediamine) cobalt(III) Perchlorate, $\text{trans-}[\text{Co}(\text{en})(\text{sdmen})(\text{NO}_2)_2] \text{ClO}_4$

Method I. A suspension of $\text{Co}(\text{NH}_3)(\text{en})(\text{NO}_2)_3$, prepared by the method of Bailor²⁵, (7.5 g, 0.27 mol) in aqueous N,N -dimethylethylenediamine (2.3 g, 0.26 mol, in 235 ml of H_2O), was heated on a steam bath for 40-45 min with occasional agitation. The resulting solution was evaporated to a past under a stream of air. This was mixed thoroughly with water (300 ml) and filtered. The filtrate was added at a rate of 1.5 ml/min to a column (diameter, 5 cm) containing one liter of strong-acid cation-exchange resin (Dowex-50-X8, 100-200 mesh) in the NH_4^+ form. Water was added at the same rate until the liquid above the column was no longer colored. The orange layer at the top of the resin was then eluted with NaClO_4 (0.075 M) over a period of 2 weeks at a rate of 0.5 ml/min. During this time the orange layer separated into six bands. The slowest three were very minor as compared to the other three. The slowest band remained at the origin, presumably composed of +2 and +3 cations. The next slowest band gave electronic and pmr spectra consistent with cis- $[\text{Co en}_2(\text{NO}_2)_2]^+$, and

the band in front of it had an electronic spectrum consistent with cis-[Co(en)(sdmen)(NO₂)₂]⁺ although it decomposed before further analysis could be performed. The fastest of the three major bands, I which was 1.8 cm wide, had moved to the bottom of the column (48 cm from the top). The next band, II, which was 6 cm wide, was not completely separated from I, but they were distinguishable because of their difference in color. Band I was brownish orange, and II was brownish yellow. The slowest of the major bands, III (colored yellow), which was 3 cm wide, had moved 31 cm from the origin. I, II, and III were removed from the column by means of a suction hose. II was removed in two portions: the 2 cm nearest to I, (labeled IIA), and the rest, (IIB). The colored material was removed from the resin of each band by elutions on small columns with NaClO₄ (0.5 N) at a rate of 4 ml/min and the eluted solutions evaporated to solids in a rotary evaporator. Each solid was re-evaporated twice with added ethanol (400 ml). The dry solids were then extracted several times with ethanol to insure complete removal of NaClO₄. I, IIA, IIB, and III yielded 0.7 g, 1.85 g, 4.4 g, and 0.9 g of solid, respectively. A thin-layer chromatography analysis of the bromide salts of I, IIA, IIB, and III along with their electronic absorption spectra showed IIB to contain the pure desired trans-[Co(en)(sdmen)(NO₂)₂]⁺ product. IIA contained a mixture of this (86%) and trans-[Co(sdmen)₂(NO₂)₂]ClO₄ as did I (6%). III was essentially trans-[Co(en)₂(NO₂)₂]ClO₄. Recrystallization of IIB from 330 ml of 50% ethanol at 55° gave large golden-brown crystals of the desired products. Anal. Calcd for [CoC₆H₂₀N₄O₄]ClO₄: C, 18.07; H, 5.07; N, 21.07. Found: C, 18.04;

H, 4.98; N, 21.20.

Method II. $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ (2.38 g), ethylenediamine (0.6 g of 98%), $\text{N,N}'$ -dimethylethylenediamine (0.88 g), NaNO_2 (1.62 g) and HCl (0.82 ml of 12.4 N) were reacted in similar manner to the preparation of trans- $[\text{Co}(\text{sdmen})_2(\text{NO}_2)_2]\text{ClO}_4$. The product was treated on an ion-exchange column as in method I. The solid isolated from bands I, IIA and IIB weighed 0.15 g, 0.32 g and 1.28 g, respectively, and had compositions similar to the products obtained in Method I.

7. Resolution of trans- $[\text{Co}(\text{en})(\text{sdmen})(\text{NO}_2)_2]\text{ClO}_4$

A solution of trans- $[\text{Co}(\text{en})(\text{sdmen})(\text{NO}_2)_2]\text{Cl}$, obtained from the ClO_4^- salt (9.1 g, 23 mmol) (see Preparation 4) was mixed vigorously with AgBCS (9.15 g, 22 mmol) and filtered to remove AgCl residue. The filtrate was evaporated to an oil and re-evaporated after 50 ml of ethanol was added. The residue was dissolved in hot ethanol (140 ml) and cooled to -20° until significant amounts of gelatinous residue formed. The mixture was then warmed with agitation to 55° until all but a small amount of the residue had dissolved. Upon cooling for 3 hours at room temperature with occasional agitation to prevent formation of gelatinous solid, large amounts of a yellow flocculent solid formed throughout the solution. The solid was collected, washed with ethanol and ether, and dried under vacuum (5.0 g, 6.5 mmol, $[\alpha]_{500} -170^\circ$ for a 0.1% solution). An additional fraction of similar activity was obtained upon cooling the filtrate to 6° (0.9 g). The first fraction was recrystallized from ethanol (250 ml) at 45° to give improved optical purity (2.2 g, $[\alpha]_{500} -210^\circ$ for 0.1% solution).

Additional recrystallization gave no further improvement in the optical purity of $(-)\text{-}_{500}\text{-trans-}[\text{Co(en)(sdmen)(NO}_2)_2]\text{BCS}$.

8. $(-)\text{-}_{\text{D}}\text{-trans-}[\text{Co(en)(sdmen)(NO}_2)_2]\text{ClO}_4$

An ethanol solution of LiClO_4 (1 g) was added dropwise to a stirred solution of $(-)\text{-}_{500}\text{-trans-}[\text{Co(en)(sdmen)(NO}_2)_2]\text{BCS}$ (2.2 g, 2.9 mmol) in about 170 ml of 95% ethanol. The desired precipitate was collected, washed with ethanol and ether, and dried under vacuum (1.15 g, $[\alpha]_{500}^{-500^\circ}$ for a 0.5% solution). Anal. Calcd for $[\text{CoC}_6\text{H}_{20}\text{N}_4\text{O}_4]\text{ClO}_4$: C, 18.07; H, 5.07; N, 21.07. Found: C, 18.09; H, 5.00; N, 21.15.

9. Inactive $\text{trans-Dichloroethylenediamine(N,N'-dimethylethylenediamine)}$ cobalt(III) Perchlorate Hemihydrate, $\text{trans-}[\text{Co(en)(sdmen)Cl}_2]\text{ClO}_4 \cdot 0.5 \text{ H}_2\text{O}$

A solution of $\text{trans-}[\text{Co(en)(sdmen)(NO}_2)_2]\text{ClO}_4$ (2 g, 5 mmol) in HCl (50 ml of 12.4 N) was heated on a steam bath for 30 min at $70\text{-}75^\circ$. The solution was evaporated to a residue on a rotary evaporator. The residue was recrystallized by dissolution in 60°HCl (25 ml of 12.4 N) and cooling to 6° . The resulting green needle-like crystals were collected, washed with cold 6N HClO_4 , ethanol and ether, and dried under vacuum. Anal. Calcd for $[\text{CoC}_6\text{H}_{20}\text{N}_4\text{Cl}_2]\text{ClO}_4 \cdot 0.5 \text{ H}_2\text{O}$: C, 18.66; H, 5.49; Cl, 28.17; N, 14.84. Found: C, 18.88; H, 5.58; Cl, 27.78; N, 14.85.

10. (+)_D-trans-Dichloroethylenediamine(N,N'-dimethylethylenediamine)
cobalt(III) Perchlorate, (+)_D-trans-[Co(en)(sdmen)Cl₂] ClO₄

A solution of (-)_D-trans-[Co(en)(sdmen)(NO₂)₂] ClO₄ (0.45 g, 1.1 mmol) in HCl (10 ml of 12.4 N) was heated for 1.5 hr at 70°. The resulting green solution was evaporated on a rotary evaporator to a residue. This was dissolved in 60° HCl (10 ml of 0.6 N), LiClO₄ (0.15 g, 7 mmol) was added with stirring, and the solution was cooled to 6° overnight. The green crystals were collected, washed with ethanol and ether, and dried under vacuum. (0.2 g, $[\alpha]_D^{+350^\circ}$ for 0.075% solution). Anal. Calcd for [CoC₆H₂₀N₄Cl₂] ClO₄: C, 19.09; H, 5.34; Cl, 28.17; N, 14.84. Found: C, 19.00; H, 5.30; Cl, 28.03; N, 15.05.

11. Conversion of (+)_D-trans-[Co(en)(sdmen)Cl₂]⁺ to (-)_D-trans-[Co(en)(sdmen)(NO₂)₂]⁺

A solution (25 ml) of (+)_D-trans-[Co(en)(sdmen)(NO₂)₂] ClO₄ (0.1%, 0.06 mmol) and NaNO₂ (1.25 g, 20 mmol) in 0.01 N HClO₄ was prepared, and the change in rotation at 500 nm was followed. After 2 days the rotation remained constant, and the absorption spectrum in the 400 nm-600 nm region was indistinguishable from that of a similar solution of (-)_D-trans-[Co(en)(sdmen)₂(NO₂)₂] ClO₄. The rotation in a 0.5 dm cell had changed from +0.19° to -0.19° during that time.

12. trans-Dinitrobis ((R)-N,N'-dimethylpropylenediamine)cobalt(III)
Perchlorate, trans-[Co(R-sdmpn)₂(NO₂)₂] ClO₄

This complex was prepared using the method described for trans- $[\text{Co}(\text{sdmen})_2(\text{NO}_2)_2]^+$ in section 1. The amounts of reactants used were: $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ (2.14 g, 9 mmol), amine, (1.88 g of 94.9%, 17.5 mmol), NaNO_2 (1.48 g, 21.4 mmol) and HCl (0.72 ml of 12 N). The reaction mixture was slowly evaporated to a paste which was chromatographed in a manner analogous to that described in section 6. After nine days of elution with NaClO_4 (0.075 M) at a rate of 1 ml/min, the brownish orange starting band had been eluted 48 cm from the origin and was about 17 cm wide. There were also some very minor bands near the origin (presumably, +2 and +3 cationic complexes). The major band was removed in three fractions with a suction hose: the 2.5 cm furthest from the origin, I, the next 7.5 cm, II, and finally, the slowest, 7.5 cm, III. The compounds were removed from the resin by elution with NaCl (about 600 ml of 1 M) at a rate of 5 ml/min. The solutions were evaporated on a rotary evaporator to solids, which were dried by evaporating twice from added ethanol (200 ml). The colored material was extracted from the solids from I, II, and III with ethanol (100 ml, 150 ml and 200 ml, respectively) leaving solid NaCl . The extracts were evaporated to solid on a rotary evaporator. The solids from I and II were re-extracted with ethanol (35 ml and 45 ml, respectively) and the extracts evaporated to dryness. The crude products from bands I, II, and III weighed 0.45 g, 1.2 g and 1.25 g, respectively. Band II was a mixture of both isomers of trans- $[\text{Co}(\text{R-sdmpn})_2(\text{NO}_2)]\text{Cl}$, according to the interpretation of the pmr spectra. Band I and III contained, respectively, the fast and the

slow isomers of trans- $[\text{Co}(\text{R-sdmpn})_2(\text{NO}_2)_2]\text{Cl}$. Band II was principally the slow isomer.

In order to obtain the analytically pure slow isomer of trans- $[\text{Co}(\text{R-sdmpn})_2(\text{NO}_2)_2]\text{ClO}_4$, a portion of the residue from band III (0.8 g) was suspended in ethanol (50 ml). To the solution was added LiClO_4 (0.5 g), the mixture was agitated periodically for 30 min and the resulting solid collected (0.35 g). It was recrystallized from ethanol (55 ml of 90%) by dissolution at 48° followed by cooling to -20° , which caused the orange solid to crystallize. The solid was collected, washed with ether and dried under vacuum (0.11 g). Anal. Calcd for $[\text{Co}(\text{C}_{10}\text{H}_{22}\text{N}_6\text{O}_4)]\text{ClO}_4$: C, 26.41; H, 6.22; N, 18.46. Found: C, 26.67; H, 6.34; N, 18.45.

Band I was rechromatographed on a small column (diameter, 3.5), eluting the band 37 cm from the origin. Three fractions were taken. The pmr of the three fractions were essentially the same, suggesting that the solid from band I was pure fast isomer. Because of the perchlorate salt for an elemental analysis.

13. trans-Dichlorobis ((R),N',N'-dimethylpropylenediamine)cobalt(III) Perchlorate, trans- $[\text{Co}(\text{R-sdmpn})_2\text{Cl}_2]\text{ClO}_4$

Slow isomer: trans- $[\text{Co}(\text{R-sdmpn})_2(\text{NO}_2)_2]\text{Cl}$ (slow isomer, 0.3 g), obtained directly from isolation of the complex from the column, was heated with HCl (10 ml of 12.4 N) at $69-70^\circ$ for 1 hr. The green solution was evaporated on a rotary evaporator to a residue. The residue was dissolved in HCl (15 ml of 1 N), and powdered LiClO_4 (0.2 g) was added to the green solution at 65° with stirring. (Crystallization

began immediately). The mixture was cooled to room temperature, and after 3 hr, the green solid was collected. It was washed with ethanol and ether and dried under vacuum (0.1 g). Anal. Calcd for $[\text{Co}(\text{C}_{10}\text{H}_{28}\text{N}_4\text{Cl}_2)]\text{ClO}_4$: C, 27.70; H, 6.51; N, 12.92. Found: C, 27.89; H, 6.56; N, 12.95.

Fast isomer: This was prepared in a manner analogous to that for the slow isomer from the chloride salt obtained from the column separation (it was shown by pmr analysis to contain an impurity of the slow isomer of 5-10%). Anal. Calcd for $[\text{Co}(\text{C}_{10}\text{H}_{28}\text{N}_4\text{Cl}_2)]\text{ClO}_4$: C, 27.70; H, 6.51; N, 12.92. Found: C, 27.12; H, 6.37; N, 12.88.

14. trans-Dinitroethylenediamine ((R)-N,N'-dimethylpropylenediamine)-cobalt(III) Perchlorate, trans- $[\text{Co}(\text{en})(\text{R-sdmpn})(\text{NO}_2)_2]\text{ClO}_4$

This complex was prepared and isolated in a manner analogous to that described for trans- $[\text{Co}(\text{en})(\text{sdmen})(\text{NO}_2)_2]^+$ in section 6, method I. The moles used of $[\text{Co}(\text{en})(\text{NH}_3)(\text{NO}_2)_2]$ (7.4 g, 27 mmol) and diamine (2.60 g, 26 mmol) were the same. The reaction mixture was eluted from a similar sized column with NaClO_4 (0.075 M) over a period of 2 weeks at a rate of 0.6 ml/min. The band structure that resulted was very similar to that found in section 6, and three major fast bands were similar in color to those found in that section. However, in this preparation, the fastest moving brownish-orange band (37 cm from the origin, presumably trans- $[\text{Co}(\text{R-sdmpn})_2(\text{NO}_2)_2]^+$) was more completely separated from the next brownish-yellow band (32.5 cm from the origin), which contained the desired trans- $[\text{Co}(\text{en})(\text{R-sdmpn})(\text{NO}_2)_2]^+$. The middle band (of the three fast moving bands) was removed in two parts

(1.25 cm furthest from the origin, IIA and the remaining 2.5 cm, IIB), and the complex was isolated as the perchlorate salt as indicated in section 6. IIA and IIB yielded 0.9 g and 2.65 g of solid, respectively. Pmr and thin-layer chromatographic analyses indicated that the material in IIA was essentially the desired trans- $[\text{Co}(\text{en})(\text{R-sdmpn})(\text{NO}_2)_2]\text{ClO}_4$ while IIB contained a small impurity of trans- $[\text{Co}(\text{en})_2(\text{NO}_2)_2]\text{ClO}_4$ in addition (about 5%). Portions of the solids were combined (0.55 g of IIA and 1.65 g of IIB) and twice recrystallized from ethanol (53 and 88 ml of 70%) by dissolution at 60° and crystallization upon cooling to 6°. After two recrystallizations, the solid (0.9 g, 2.2 mmol) showed no indication of trans- $[\text{Co}(\text{en})_2(\text{NO}_2)_2]^+$ impurity. Anal. Calcd for $[\text{Co}(\text{C}_7\text{H}_{22}\text{N}_6\text{O}_4)]\text{ClO}_4$: C, 20.37; H, 5.37; N, 20.36. Found: C, 20.05; H, 5.34; N, 20.39.

15. trans-Dichloroethylenediamine ((R)-N,N'-dimethylpropylenediamine)-cobalt(III) Perchlorate, trans- $[\text{Co}(\text{en})(\text{R-sdmpn})\text{Cl}_2]\text{ClO}_4$

This was prepared by a method analogous to that described in section 10 for (+)_D-trans- $[\text{Co}(\text{en})(\text{sdmen})\text{Cl}_2]\text{ClO}_4$. Anal. Calcd for $[\text{Co}(\text{C}_7\text{H}_{22}\text{N}_4\text{Cl}_2)]\text{ClO}_4$: C, 21.47; H, 5.66; N, 14.31; Cl, 27.16. Found: C, 21.79; H, 5.59; N, 14.16; Cl, 27.24.

16. trans-Dinitro ((R)-propylenediamine)((R)-N,N'-dimethylpropylenediamine)cobalt(III) Perchlorate, trans- $[\text{Co}(\text{R-pn})(\text{R-sdmpn})(\text{NO}_2)_2]\text{ClO}_4$

This complex was prepared and chromatographed by the method for the preparation of trans- $[\text{Co}(\text{en})(\text{sdmen})(\text{NO}_2)_2]^+$ (section 6, method II). $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ (5.5 g, 23 mmol), (R)-propylenediamine (1.73 g, 23 mmol),

(R)-N,N -dimethylpropylenediamine (2.37 g, 23 mmol), NaNO_2 (3.53 g, 50 mmol) and HCl (1.9 ml of 12.3 N) were reacted, and the reaction residue was put on two columns (diameter, 5 cm). After thirteen days of elution with NaClO_4 (0.075 M) at a rate of 0.8 ml/min, the fastest band had moved 49 cm from the origin. The band structure was comparable to the three major bands found in section 6 except that there was not a distinct color separation between what was in section 6 the two slower bands. In subsequent discussions, this region is designated in total as band II. The fastest band, designated I, which was brownish orange, was about 2 cm thick and was distinguished from band II, which was 15 cm thick, by the difference in color: band II ranged in color from brownish-yellow at the interface with band I to yellow at the top. The only other bands were minor bands at 5 and 10 cm from the origin (presumably cis dinitrobis(diamine) complexes) and a red band at the origin. Band I was removed in one part, and band II was removed in six parts from the column (designated IIA-IIF with IIA the fastest fraction). Each fraction was 2.5 cm thick. The product was eluted from each fraction with NaCl as described in section 12 for trans- $[\text{Co}(\text{R-sdmpn})_2(\text{NO}_2)_2]^+$. The final residues of the chloride salts of the complex resulted from the evaporation of 100 ml ethanol extracts. The residues from I and IIA-IIF weighed 0.55 g and 1.5 g, 1.2 g, 1.05 g, 0.7 g, 0.45 g and 0.25 g, respectively. On the basis of pmr analysis of the N-methyl peaks, band I contained trans- $[\text{Co}(\text{R-sdmpn})_2(\text{NO}_2)_2]^+$ (about 30%, both isomers) and trans- $[\text{Co}(\text{R-pn})(\text{R-sdmpn})(\text{NO}_2)_2]^+$ (fast isomer). Band IIA was exclusively trans- $[\text{Co}(\text{R-pn})(\text{R-sdmpn})(\text{NO}_2)_2]^+$ (fast isomer). Band IIB appeared

to be fast isomer with a small impurity of the slow isomer. Band IIC appeared to be a mixture of the fast and slow isomers and bands IID-IIF contained predominantly the slow isomer. However, tlc analysis showed a small impurity of trans- $[\text{Co}(\text{R-pn})_2(\text{NO}_2)_2]^+$ in band IIF.

In order to obtain the pure perchlorate salt of trans- $[\text{Co}(\text{R-pn})(\text{R-sdmpn})(\text{NO}_2)_2]^+$ (fast isomer), solid from band IIA (1.45 g) was dissolved in ethanol (25 ml), and a LiClO_4 solution (0.5 g in 6 ml of ethanol) was added dropwise with stirring to the solution. The resulting yellow solid was filtered, washed with ethanol (5 ml) and dried (1.23 g). Part of this solid (0.8 g) was recrystallized once from ethanol (53 ml of 96%) by dissolution at 43° and cooling to 6° . The small yellow crystals were collected; washed with ethanol and ether; and dried under vacuum. Anal. Calcd for $[\text{Co}(\text{C}_8\text{H}_{24}\text{N}_6\text{O}_4)]\text{ClO}_4$: C, 22.50; H, 5.67; N, 19.67. Found: C, 22.40; H, 5.67; N, 19.67. Found: C, 22.40; H, 5.51; N, 19.47.

The slower isomer was obtained by chromatographing 1.6 g of bands IID and IIIE on a column (diameter, 4 cm) in a manner similar to the first separation. The resulting band was eluted to 45 cm from the origin where it was 15 cm wide. The slower 11 cm of the band was removed, and the solid was obtained as above. It contained 0.74 g of extracted solid while the faster 4 cm contained 0.5 g. The slow fraction also contained a small amount of green impurity, presumably trans- $[\text{Co}(\text{R-pn})(\text{R-sdmpn})\text{Cl}_2]^+$. This was almost completely removed when the residue, dissolved in ethanol (15 ml), was treated with a LiClO_4 solution (0.2 g in 2 ml of ethanol). The green solid precipitated first. The solution was decanted after a few minutes, and

the yellow solid, which then crystallized, was free of green impurity. After cooling to 6°, this solid was collected; washed with ethanol (1 ml) and ether; and dried under vacuum (0.5 g). The fast isomer was not detected by pmr analysis as an impurity in this fraction, and it was assumed to be pure trans-[Co(R-pn)(R-sdmpn)(NO₂)₂]ClO₄ (slow isomer). A sample for elemental analysis was not prepared for this solid because of the limited quantity available.

17. trans-Dichloro ((R)-propylenediamine)((R)-N,N'-dimethyl-propylene-diamine)cobalt(III) Perchlorate, trans-[Co(R-pn)(R-sdmpn)]Cl₂ ClO₄

Fast isomer: This was prepared in a manner analogous to that of (+)_D-trans-[Co(en)(R-sdmpn)Cl₂]ClO₄ described in section 6. Anal. Calcd for [Co(C₈H₂₄N₄Cl₂)]ClO₄: C, 23.60; H, 5.97; N, 13.82. Found: C, 23.60; H, 5.94; N, 13.83.

Slow isomer: This was prepared similar to the fast isomer. Anal. Calcd for [Co(C₈H₂₄N₄Cl₂)]ClO₄: C, 23.60; H, 5.97; N, 13.82; Cl, 26.20. Found: C, 23.34; H, 5.90; N, 13.98; Cl, 26.10.

18. trans-Dinitro ((S)-propylenediamine)((R)-N,N'-dimethylpropylene-diamine)cobalt(III) Chloride, trans-[Co(S-pn)(R-sdmpn)(NO₂)₂]Cl

CoCl₂·6 H₂O (8.32 g, 35 mmol), (S)-propylenediamine (2.59 g, 35 mmol), NaNO₂ (5.31 g, 77 mmol) and HCl (2.85 ml of 12.3 N) were reacted following the method of preparation for trans-[Co(en)(sdmen)(NO₂)₂]ClO₄, and the reaction mixture was chromatographed on a column (diameter, 6.75 cm) as described in section 6. After thirteen days of elution at a rate of 1.2 ml/min, three major bands with colors

similar to those found in section 6 were formed (also, a band at the origin and three slow minor bands, presumably three cis-[Co(daimine)(NO₂)₂]⁺ complexes, were found). The leading edge of the three major bands was 41.5 cm from the origin and their total thickness was 21 cm. The two faster bands were considerably overlapped. Superimposed on the slow band and the trailing edge of the middle band was an additional band. Because of the considerable overlapping of the major bands, this part of the column was taken in five fractions (designated I-V, starting at the front). The complexes were isolated from these fractions as the chloride salts following the method outlined in section 16. The solids isolated from bands I-V weighed 1.95 g, 2.0 g, 1.35 g, 2.05 g and 1.0 g, respectively. Band I (3.5 cm thick), which was about 70% of the fastest brownish orange band, contained exclusively trans-[Co(R-sdmpn)₂(NO₂)₂]⁺ (both isomers). Band II (4.5 cm thick) contained the rest of the brownish orange band and about 50% of the next band (brownish yellow), and it consisted of trans-[Co(R-sdmpn)₂(NO₂)₂]⁺ (slow isomer) and the fast isomer of trans-[Co(S-pn)(R-sdmpn)(NO₂)₂] (about 60%). Band III (4.2 cm), which was almost all of the remaining brownish yellow band, contained principally the slow isomer of trans-[Co(S-pn)(R-sdmpn)(NO₂)₂]⁺ as well as some trans-[Co(R-sdmpn)₂(NO₂)₂] (slow isomer, 20%). Band IV (3.7 cm) consisted of the band that had not been found in the preparations of the other dinitro complex of two diamines (in sections 6, 12 and 16). This band contained much trans-[Co(S-pn)₂(NO₂)₂]⁺ (according to tlc analysis) as well as some other compounds giving faster tlc spots. Pmr analysis of this band was not too informative. Band V

(3.7 cm) was essentially trans- $[\text{Co}(\text{S-pn})_2(\text{NO}_2)_2]^+$.

Band IV was rechromatographed on a column. After two weeks of elution, significant sized slow and fast bands developed as were found in the initial separation, suggesting that the initial band had decomposed to a large extent upon work-up as the chloride salt.

Bands II and III were rechromatographed in order to obtain pure fast and slow isomers, respectively, of the desired product. In each case, the final broad band was taken in several fractions. Although each isomer was obtained free from the other isomer, both isomers still contained detectable amounts of trans- $[\text{Co}(\text{R-sdmpn})(\text{NO}_2)_2]$. Recrystallization of these fractions as the perchlorate salts did not remove these impurities.

D. Conversion of Perchlorate Salts to Bromide and Chloride Salts

For proton magnetic resonance measurements, all slightly soluble perchlorate salts were converted to more soluble chloride salts by thoroughly mixing aqueous suspensions of perchlorate salts (1 N HCl suspensions for the dichloro complexes) with equimolar amounts of tetraphenylarsonium chloride. The solutions were filtered and evaporated to dryness. Chloride salts used in resolutions were obtained by passing the perchlorate salts through a column of a strong-base anion-exchange resin (Dowex 1-X8, 50-100 mesh) in the Cl^- form, which had sufficient resin such that the exchange capacity of the column was in 40-50 fold excess. The solutions were then evaporated on a rotary evaporator to the desired solids. Similarly, the bromide salts for thin-layer chromatography were prepared using resin in the Br^- form.

E. Thin-layer Chromatography

The plates used (10 cm x 20 cm or 20 cm x 20 cm) were coated with Cellex-N1 TLC cellulose (~0.5 mm thick). Some precoated plates (0.25 mm thick) were used (produced by Quantum Ind., Fairfield, N.J.). Sample applications were made with aqueous solutions (1-2 l) of the complex bromide salts (100-150 g). The plates were developed, using a Brinkman development tank with a solvent system suggested for nitro-amine complexes by MacDermott²⁶ (butanol, pyridine, water, acetic acid, 40%:30%:20%:10%).

F. Electronic Absorption Spectra

Spectra were recorded at room temperature using a Cary Model 14 spectrophotometer and 0.05%-0.1% solutions (0.001%-0.002% in the uv region) in 1 cm or 5 cm quartz cells. The slit was run by program with the dynode at a setting of 2 and the slit control at a setting of 20.

G. Optical Rotations

Rotations were measured at room temperature using a Beckman Model DU-2 spectrophotometer with a Keston Model D polarimetric attachment (Standard Polarimeter Co., Hackensack, New Jersey) and 0.05%-0.1% solutions in 5 cm or 1 cm quartz cells. All measurements of dinitro complexes were performed on 10^{-3} M HClO_4 solutions. Measurements of dichloro complexes were performed on methanol solutions. The slit was set at 0.4 mm.

H. Circular Dichroism Spectra

Spectra was recorded at room temperature using a Cary Model 60 spectropolarimeter with a CD attachment. Sample concentrations were 0.05%-0.1% in the visible region and 0.001%-0.002% in the uv region. The slit was run by program below 580 nm and at a setting of 0.2 mm above 580 nm.

I. Proton Magnetic Resonance Spectra

Spectra were recorded either on a Varian A-60 or HA-100 spectrometer with sodium trimethylsilylpropanesulfonate as an internal standard. Spectra were measured, using D₂O solutions or D₂O-DCI solutions, 4%-20% in complex. N-deuterated samples were obtained by allowing D₂O solutions of the complexes to sit for several hours.

J. Analysis of the PMR Spectrum of trans-[Co(sdmn)₂(NO₂)₂]Cl

The methylene portion of the 60 MHz pmr spectra of the N-deuterated complex was analyzed using the LAOCN3 iterative program written by A.A. Bothner-By²⁷ which was modified for use by the Upjohn Company, Kalamazoo, Michigan, for an IBM 360/30 computer. Calculated spectra were plotted using their EAI-3500 Dataplotter. By trial and error, an AA'BB' spectrum was calculated which approximated the experimental spectrum sufficiently to make line assignments. The experimental line assignments were then used to calculate a best fit spectrum. Additional modification of the calculated spectrum was achieved by correction for long-range coupling of the methylene protons with the

N-CH₃ protons; this was not iterated, but arrived at by trial and error using band shape as the main criteria.

K. Hydrogen Exchange Studies

Rates of hydrogen exchange in $(-)_D$ -trans-[Co(en)(sâmen)(NO₂)₂]Cl were measured with the use of a Varian A-60 spectrometer by observing the coalescence of the N-methyl doublet into a singlet. All studies were performed at 34.3°. Samples were maintained at 34.3° ± 0.1° in a pmr sample tube by thermostating the tube in a constant temperature bath between measurements. Pmr measurements were made rapidly (1-2 min), and samples were then quickly returned to the bath. The pmr probe temperature was about 32°.

The reactions were run in deuterium oxide solutions in which the pH was adjusted with 0.2 M acetate buffer (described in detail elsewhere²), and the ionic strength was maintained with 1M KCl. The pH of the deuterium oxide buffer solutions was measured with a Beckman Expandomatic pH meter and a Beckman miniature combination electrode. pD values were calculated from the empirical formula, $pD = pH + 0.4$.^{28,29} Standardized buffers were stored in septum bottles. Solution concentrations were 4%. The peak height of the acetate signal from the buffer was used to correct for small variations of the resolution of the instrument with time. The exchange reactions were followed for 2 to 3 half-lives for all except the slowest reaction (half-life 19 hr), which was for 1.5 half-lives.

L. Loss of Optical Activity Studies

Rates of loss of optical activity of $(-)_D\text{-trans-}[\text{Co(en)(sdmen)}(\text{NO}_2)_2]\text{ClO}_4$ were followed in the polarimeter described in Section G. Samples were contained in a 1 dm jacketed cell. The temperature was maintained at $34.3^\circ \pm 0.1^\circ$ with a constant temperature circulating bath. Samples were dissolved in 0.05 M glycine-NaOH buffered solutions in which the ionic strength was maintained with 0.5M or 1M KCl. The pH of these buffers were measured initially both at room temperature and 34.3° , using a Beckman Research pH meter and electrodes. Subsequent buffers were then measured only at room temperature, and the pH were calculated for 34.3° . Solution concentrations varied from 0.03% to 0.1%. Changes in rotation were measured in the region of 390-540 nm, but the rate constants were generally evaluated in the region of 500-510 nm. In this region, initial rotations were from 0.15° to 0.36° , and reactions were followed for 2-4 half-lives.

M. Hydrolysis Studies

Rates of hydrolysis of $(-)_D\text{-trans-}[\text{Co(en)(sdmen)}(\text{NO}_2)_2]\text{ClO}_4$ were followed by observing the change in absorbance at the low energy maxima of the complex (446 nm), using a Cary model 14 recording spectrometer. The samples were contained in 0.5 dm and 1 dm quartz cells that were externally jacketed. The jackets were maintained at 34.3° , using a constant temperature circulating bath that maintained the temperature within ± 0.1 . The pH of the solutions were adjusted with the buffers used in Section L. The reactions were followed for

1.5-2.5 half-lives.

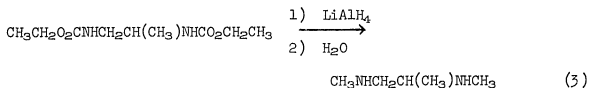
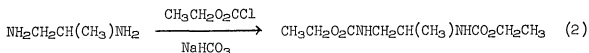
N. Analyses

All elemental Analyses were performed by Midwest Microlab, Indianapolis, Indiana, and Galbraith Laboratories, Knoxville, Tennessee.

V. RESULTS AND DISCUSSION

A. Preparations

The ligand, (R)-N,N'-dimethylpropylenediamine (R-sdmpn), was readily prepared from (R)-propylenediamine in two steps as summarized in equations 2 and 3. Recently, the enantiomer, S-sdmpn, was prepared



from L-alanine by Saburi, et al.¹⁰

Table I summarizes the dinitro complexes prepared in this study and the stereoisomers identified. The complexes, trans-[Co(sdmen)₂(NO₂)₂]⁺ and trans-[Co(R-sdmpn)₂(NO₂)₂]⁺, were prepared using the method of Buckingham, et al.³ for the analogous complexes of N-methylethylenediamine (men). When Co⁺², diamine, NaNO₂ and HCl were allowed to react in the mole ratio, 1:2:2:1, the main impurities were the green trans dichloro complexes, trans-[Co(dimine)₂Cl₂]⁺. If the relative moles of NaNO₂ was increased to 2.3, the green impurity was eliminated but was replaced by anionic impurities (presumably, [Co(diamine)(NO₂)₄]⁻, and [Co(NO₂)₆]³⁻). The preparation of the enantiomer of the bis(R-sdmpn) complex in which S-sdmpn is reacted with Na₃[Co(NO₂)₆], was reported recently.¹⁰ It was stated by these authors that this complex could not be prepared by the above air

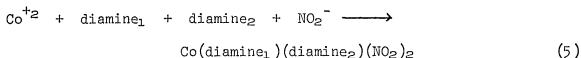
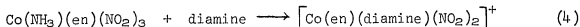
TABLE I
 Stereoisomers of trans- $[\text{Co}(\text{diamine})_2(\text{NO}_2)_2]^+$
 Prepared and Identified

Complex Ion	Number of Stereoisomers
$[\text{Co}(\text{sdmen})_2(\text{NO}_2)_2]^+$	2 ^a
$[\text{Co}(\text{en})(\text{sdmen})(\text{NO}_2)_2]^+$	2 ^a
$[\text{Co}(\text{R-sdmpn})_2(\text{NO}_2)_2]^+$	2 ^{b,c}
$[\text{Co}(\text{en})(\text{R-sdmpn})(\text{NO}_2)_2]^+$	1
$[\text{Co}(\text{R-pn})(\text{R-sdmpn})(\text{NO}_2)_2]^+$	2 ^{b,d}
$[\text{Co}(\text{S-pn})(\text{R-sdmpn})(\text{NO}_2)_2]^+$	2 ^{b,c}

^aExist as a dl pair. ^bExist as positional diastereomers that arise because of the C-methyl substituents. ^cMajor positional diastereomer is the one having the lesser mobility on cationic-exchange resin. ^dMajor positional diastereomer is the one having the more rapid mobility on cationic-exchange resin.

oxidation method although we found that the reaction proceeded in the expected manner.

Two methods were used to prepare the dinitro mixed(diamine) complexes of sdmen and R-sdmpn with ethylenediamine (en) and propylenediamine (pn) as outlined in equations 4 and 5. Both methods gave



trans- $[\text{Co}(\text{en})(\text{sdmen})(\text{NO}_2)_2]^+$, in comparable yields (40-50%). Each preparation produced similar yields of the trans dinitrobis(diamine) complexes of en and sdmen (5-10%) and the analogous cis complexes, $[\text{Co}(\text{en})(\text{sdmen})(\text{NO}_2)_2]^+$ and $[\text{Co}(\text{en})_2(\text{NO}_2)_2]^+$, as well. The reaction of $\text{Co}(\text{NH}_3)(\text{en})(\text{NO}_2)_3$ with sdmen is comparable to the reaction with R-pn²⁶ in that each produces significant amounts of disproporation products.

The other dinitro mixed(diamine) complexes with the exception of trans- $[\text{Co}(\text{S-pn})(\text{R-sdmpn})(\text{NO}_2)_2]^+$, were prepared in yields comparable to $[\text{Co}(\text{en})(\text{sdmen})(\text{NO}_2)_2]^+$. The relative amounts of the bis(diamine) complex impurities were small.

Three of the dinitro complexes of R-sdmpn were found to exist in two forms (see Table I). These forms were found to be diastereomers which arise because the C-methyl substituents on each diamine are situated on carbons adjacent to amine nitrogens which can be (1) across from each other (trans) or (2) adjacent to each other (cis). Hereafter, these forms will be referred to as positional diastereomers,

and they will be designated (along with the dichloro derivatives) by their relative rates of elution on cation-exchange resin as fast and slow isomers (f-isomer and s-isomer). These isomers were obtained reasonably pure for the bis(R-sdmpn) complex and for the mixed complex of R-sdmen and R-pn. However, in the preparation of trans- $[\text{Co}(\text{S-pn})(\text{R-sdmpn})(\text{NO}_2)_2]^+$, the two bis(diamine) complexes were the major products and the desired mixed complex was minor. Because of this, neither mixed diastereomer was obtained in pure form, separated from the bis(R-sdmpn) complex, although they were obtained reasonably pure from each other. This change in yield of the mixed complex is not too surprising. It appears to be related to the interactions of the two gauche diamine rings with each other (this will be discussed in more detail in Section D along with the positional isomerism).

The dinitro complexes of sdmen, which were isolated as enantiomeric pairs, were readily resolved by crystallization as the α -bromocamphor- π -sulfonate salt (BCS). In each case the levo complex salt was less soluble and crystallized first. No more than two recrystallizations were needed to obtain each optically pure. In fact, it was very difficult to obtain the more soluble dextro complex as a solid.

The dichloro complexes were obtained from each dinitro complex with the exception of the mixed complex of R-sdmpn and S-pn, which was not obtained free of the bis (R-sdmpn) complex. In all cases, the dichloro complexes were prepared from a treatment of the dinitro complexes with concentrated HCl at 70°. Saburi, et al.¹⁰ reported that the enantiomer of trans- $[\text{Co}(\text{R-sdmpn})_2\text{Cl}_2]^+$ could not be prepared

in their laboratories by this method or by other methods attempted. However, we encountered no unusual difficulty in this preparation.

When optically active trans- $[\text{Co}(\text{en})(\text{sdmen})\text{Cl}_2]^+$ was converted back to the dinitro complex, it retained 84% of its activity. This is similar to the results found with $(-)_D$ -trans,trans- $[\text{Co}(\text{men})_2(\text{NO}_2)_2]^+$ which retained 90% of its activity.⁶ Trans- $[\text{Co}(\text{sdmen})_2\text{Cl}_2]^+$, on the other hand, lost none of its activity. Racemization of the other complexes was not possible because of the stereospecificity of optically active R-sdmpn.

B. Spectra

1. Circular dichroism and uv-visible spectra

The uv-visible absorption spectra and circular dichroism for the dinitro and dichloro complexes of sdmen are given in Figures 8 and 9, respectively. Their band locations and intensities are tabulated in Table II. The analogous results for the complexes of R-sdmpn are given in Figure 10 and 11 and Table III. For the dichloro complexes, although CD and absorption curves for both f and s-isomers were recorded, only one form is shown because of the similarity.

The CD curves will be discussed in detail in later sections. The low energy absorption band near $22,000\text{ cm}^{-1}$ for trans- $[\text{Co}(\text{sdmen})_2(\text{NO}_2)_2]^+$, trans- $[\text{Co}(\text{en})(\text{sdmen})(\text{NO}_2)_2]^+$ and trans- $[\text{Co}(\text{en})_2(\text{NO}_2)_2]^+$ ($23,100\text{ cm}^{-1}$) shows a band shift to higher energy of $350\text{--}400\text{ cm}^{-1}$ for each N-methyl substituent removed. The two bands near $29,000\text{ cm}^{-1}$ and $40,000\text{ cm}^{-1}$ were not as sensitive to

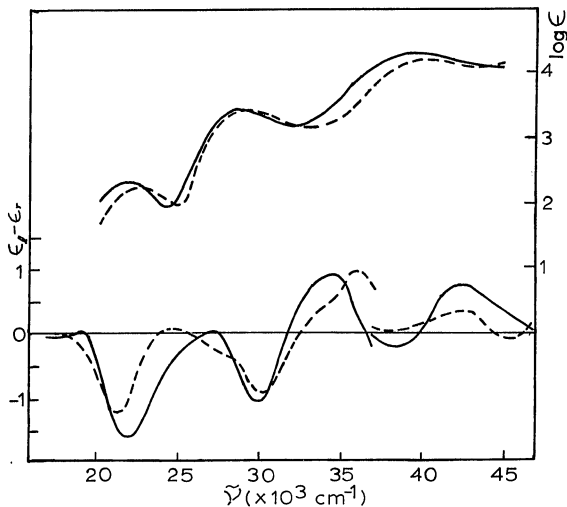


Figure 8. The absorption and CD spectra for $(-)_D\text{-trans-}[\text{Co}(\text{sdmen})_2(\text{NO}_2)_2]^+$ (—), and $(-)_D\text{-trans-}[\text{Co}(\text{en})(\text{sdmen})(\text{NO}_2)_2]^+$ (---).

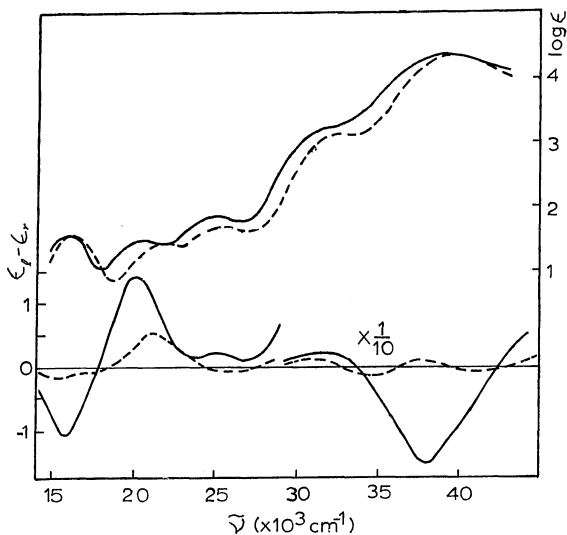


Figure 9. The absorption and CD spectra for $(+)\text{D-trans-[Co(sdmen)}_2\text{Cl}_2]^+$ (—), and $(+)\text{D-trans-[Co(en)(sdmen)Cl}_2]^+$ (---).

TABLE II
Electronic Absorption and Circular Dichroism
Data of Complexes of sdmen^a

Complex Ion	<u>Absorption</u>		<u>CD</u>	
	$\sqrt{\epsilon}_{\max}$	ϵ_{\max}	$\sqrt{\epsilon}_{\max}$	$\Delta\epsilon_{\max}^e$
$(-)_D$ - <u>trans</u> - $[\text{Co}(\text{sdmen})_2(\text{NO}_2)_2]^+{}^b$	21.6	234	18.9	+0.01
	28.6	3080	21.9	-1.62
	39.1	21,800	27.0	+0.05
	48.5	13,400	29.8	-1.07
			34.4	+0.93
			38.2	-2.2
			42.4	+7.5
$(-)_D$ - <u>trans</u> - $[\text{Co}(\text{en})(\text{sdmen})(\text{NO}_2)_2]^+{}^b$	22.4	189	21.4	-1.23
	29.0	2980	24.5	+0.07
	39.5	17,600	30.3	-0.92
	48.1	18,600	36.2	+0.96
			42.6	+3.9
$(+)_D$ - <u>trans</u> - $[\text{Co}(\text{sdmen})\text{Cl}_2]^+{}^c$			45.4	-0.7
	15.6	34.1	15.8	-1.07
	20.4	29.0	20.0	+1.42
	24.6	69.8	25.2	+0.22
	31.6 ^d	1680	31.8	+2.3
	38.8	24,760	37.9	-15
$(+)_D$ - <u>trans</u> - $[\text{Co}(\text{en})(\text{sdmen})\text{Cl}_2]^+{}^c$	16.1	33.1	15.3	-0.17
	21.5	24.0	21.1	+0.52
	25.4	48.8	25.6	-0.05
	31.4	1250	31.2	+1.3
	39.2	23,500	37.7	+0.8
			40.8	-0.5

^aAll energies in 10^3 cm^{-1} . ^bIn 10^{-3} M HClO_4 . ^cIn methanol. ^dShoulder.
^e $\Delta\epsilon$ ($1 \text{ cm}^{-1} \text{ mol}^{-1}$) = $[\theta]/3298$ ($\text{deg cm}^{-1} \text{ mol}^{-1}$ ml x 10), where $[\theta]$ is the molar ellipticity.

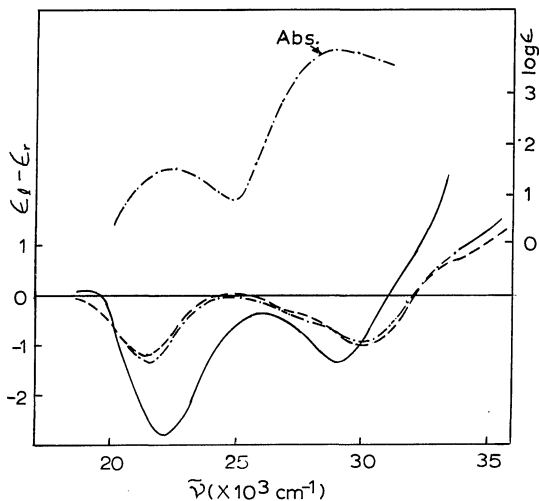


Figure 10. Absorption and CD spectra for $\text{trans-}[\text{Co}(\text{R-sdmpn})(\text{NO}_2)_2]^+$, s -isomer (—), $\text{trans-}[\text{Co}(\text{en})(\text{R-sdmpn})(\text{NO}_2)_2]^+$ (---), and $\text{trans-}[\text{Co}(\text{R-pn})(\text{R-sdmpn})(\text{NO}_2)_2]^+$, f -isomer (-.-).

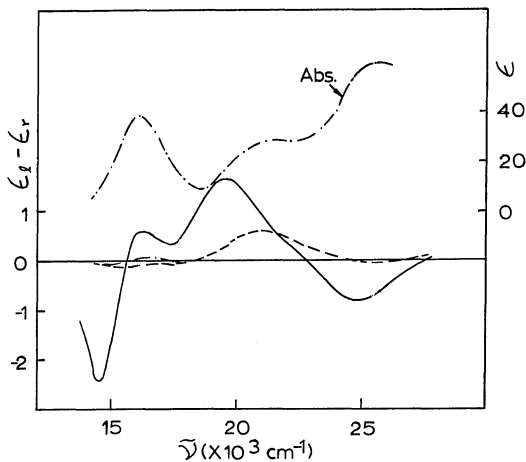


Figure 11. Absorption and CD spectra for $\text{trans-}[\text{Co}(\text{R-sdmpn})\text{Cl}_2]^+$, s-isomer (—), $\text{trans-}[\text{Co}(\text{en})(\text{R-sdmpn})\text{Cl}_2]^+$ (---) and $\text{trans-}[\text{Co}(\text{R-pn})(\text{R-sdmpn})\text{Cl}_2]^+$, f-isomer (-.-).

TABLE III

Electronic Absorption and Circular Dichroism
Data of Complexes of R-sdmpn^a

Complex Ion	Absorption		CD	
	ν_{\max}	ϵ_{\max}	ν_{\max}	$\Delta \epsilon^g$
<u>trans</u> -[Co(R-sdmpn) ₂ (NO ₂) ₂] ⁺ ^b (s-isomer)	21.7	275	19.2	+0.14
	28.7	2500	21.6	-2.77
	39.4	23,600	29.2	-1.32
	49.2	13,200	36.5	+5.1
			42.0	+14
<u>trans</u> -[Co(en)(R-sdmpn)(NO ₂) ₂] ⁺ ^b	22.4	182	21.4	-1.23
	29.1	3090	24.8	+0.02
	39.4	19,800	30.1	-1.0 ^e
	47.8	17,950		
<u>trans</u> -[Co(R-pn)(R-sdmpn)(NO ₂) ₂] ⁺ ^b (f-isomer)	22.4	184	21.5	-1.32
	29.0	2870	30.0	-0.96 ^e
	39.7	19,500		
	47.9	18,100		
<u>trans</u> -[Co(R-sdmpn) ₂ Cl ₂] ⁺ ^c (s-isomer)	15.2	52.5	14.6	-2.37
	19.7	30.1	16.3	+0.53
	24.3	81.9	19.6	+1.59
			24.9	-0.81 ^f
<u>trans</u> -[Co(R-sdmpn) ₂ Cl ₂] ⁺ ^c (f-isomer)	15.2	52.5	14.5	-2.42
	19.7	29.6	16.3	+0.57
	24.2	81.4	19.6	+1.62
			24.8	-0.83 ^f
<u>trans</u> -[Co(en)(R-sdmpn)Cl ₂] ⁺ ^e	16.1	38.8	15.3	-0.13
	21.4	27.4	21.1	+0.59
	25.4	55.9	25.6	-0.04
	33.1 ^d	2010	31.0	+1.2
	39.4	22,900	34.7	-1.0
			37.7	+1.2

TABLE III (continued)

Complex Ion	Absorption		CD	
	ν_{\max}	ϵ_{\max}	ν_{\max}	$\Delta \epsilon$
<u>trans</u> -[Co(R-pn)(R-sdmpn)Cl ₂] ⁺ ^c (s-isomer)	16.1	37.5	14.8	-0.09
	21.3	28.1	16.3	+0.02
	25.8	58.6	17.5	-0.02
	33.0 ^d	2130	21.0	+0.62
	39.4	21,000	25.8	-0.08
			30.9	+0.9
			34.7	+1.0
<u>trans</u> -[Co(R-pn)(R-sdmpn)Cl ₂] ⁺ ^c (f-isomer)	16.1	37.9	14.9	-0.10
	21.4	27.5	16.4	+0.03
	25.3	54.4	17.8	-0.02
	32.1 ^d	1860	21.1	-0.63
	39.4	18,600	25.8	-0.09
			31.1	+0.6
			34.6	-2.0
			39.2	+0.6
			40.5	-0.8

^aAll energies in 10³ cm⁻¹. ^bIn 10⁻³ M HClO₄. ^cIn methanol. ^dShoulder.

^eRecorded up to 36,000 cm⁻¹. ^fRecorded up to 37,000 cm⁻¹.

^g $\Delta \epsilon$ (l cm⁻¹ mol⁻¹) = $[\theta]/3298$ (deg cm⁻¹ mol⁻¹ ml x 10), where $[\theta]$ is the molar ellipticity.

such structural changes. A similar shift was observed for the bands near $22,000\text{ cm}^{-1}$ for the dichloro complexes (about 500 cm^{-1} shift per methyl in each case). The position of the absorption band maxima of the C-methyl substituted complexes were approximately the same as the analogous unsubstituted complexes in all cases. Thus, N-methyl substitution, when compared to C-methyl substitution, plays a more important role in modifying the ligand field strength of ethylenediamine, at least as it is manifest by uv-visible band shifts.

2. Proton magnetic resonance

Pmr spectral assignments for the complexes of sdmen are tabulated in Table IV, and those for the complexes of R-sdmpn are tabulated in Table V. The pmr spectrum for trans- $[\text{Co}(\text{sdmen})(\text{NO}_2)_2]^+$, on which a detailed spectral analysis was performed, is shown in Figure 12.

The active dinitro complexes of sdmen exhibit pmr spectra that are indistinguishable from those of the inactive forms from which they were resolved. In general the complexes of sdmen give single sharp N-methyl doublets (sharp singlets when the amine protons were deuterated) and complex multiplets for the methylene portions. The amine protons were assigned symmetric signals that are downfield from the primary amine protons of ethylenediamine.

Most of the complexes of R-sdmpn give two resolved N-methyl resonances (doublets; singlets when the amine protons are exchanged with deuterium). This is expected, for the N-methyl substituents are not equivalent even in the free amine because of the C-methyl substituent. The C-methyl exhibits one doublet in each bis (R-sdmpn)

TABLE IV

Assignment of Chemical Shift (PPM)^a for
PMR Spectra of Complexes of Sdmen

Complex Ion	N-CH ₃	-CH ₂ -	-NH ₂	=NH
<u>trans</u> -[Co(sdmen) ₂ (NO ₂) ₂] ⁺ ^b	2.20	2.3 - 3.3		5.8
<u>trans</u> -[Co(en)(sdmen)(NO ₂) ₂] ⁺ ^b	2.27	2.4 - 3.2	5.3	5.9
<u>trans</u> -[Co(sdmen) ₂ Cl ₂] ⁺ ^c	2.43	2.5 - 3.4		5.9
<u>trans</u> -[Co(en)(sdmen)Cl ₂] ⁺ ^c	2.46	2.6 - 3.3	5.6	5.9

^aSodium trimethylsilylpropanesulfonate as internal standard reference.
^bIn 0.01 N DCl. ^cIn 0.1 N DCl.

TABLE V
Assignment of Chemical Shift (PPM)^a for PMR Spectra of Complexes of R-sdmpn

Complex Ion	N-CH ₃	C-CH ₃	=CHCH ₂ -	-NH ₂ and/or =NH
<u>trans</u> -[Co(R-sdmpn) ₂ (NO ₂) ₂] ⁺ b				
(f-isomer)	2.12, 2.16	1.38	2.2-3.2	
(s-isomer)	2.15	1.38	2.2-3.2	
<u>trans</u> -[Co(R-pn)(R-sdmpn)(NO ₂) ₂] ⁺ b				
(f-isomer)	2.22, 2.25	1.37	2.3-3.3	5.1, 5.5, 5.9
(s-isomer)	2.20, 2.26	1.37	2.3-3.3	5.1, 5.3, 5.9
<u>trans</u> -[Co(S-pn)(R-sdmpn)(NO ₂) ₂] ⁺ c				
(f-isomer)	2.29, 2.36	1.22, 1.33	e	e
(s-isomer)	2.32, 2.37	1.22, 1.32	e	e
<u>trans</u> -[Co(en)(R-sdmpn)(NO ₂) ₂] ⁺ b	2.23, 2.28	1.37	2.3-3.5	5.1, 5.4, 6.1
<u>trans</u> -[Co(R-sdmpn) ₂ Cl ₂] ⁺ d				
(f-isomer)	2.38	1.38	2.5-3.5	5.5, 6.1
(s-isomer)	2.35, 2.38	1.37	2.5-3.5	5.5, 6.2

TABLE V (Continued)

Complex Ion	N-CH ₃	C-CH ₃	=CHCH ₂ -	-NH ₂ and/or =NH
<u>trans</u> -[Co(R-pn)(R-sdmpn)Cl ₂] ⁺ ^d				
(f-isomer)	2.39, 2.42	1.39	2.5-3.5	4.9-6.2
(s-isomer)	2.42	1.39, 1.41	2.5-3.7	4.9-6.2
<u>trans</u> -[Co(en)(R-sdmpn)Cl ₂] ⁺ ^d	2.44	1.38	2.6-3.4	4.9-6.4

^aSodium trimethylsilylpropanesulfonate as internal standard reference. ^bIn 0.1 N DCl.

^cN-deuterated in D₂O. ^dIn 0.1 N DCl. ^eNot measured because the complex contained [Co(R-sdmpn)₂(NO₂)₂]⁺ impurity.

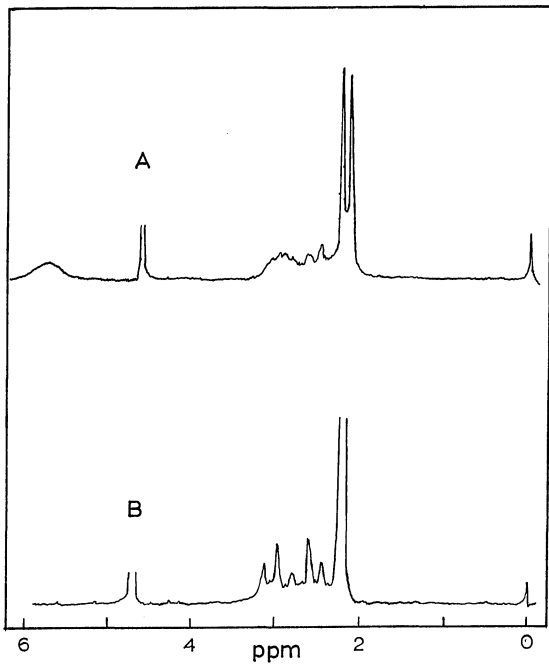
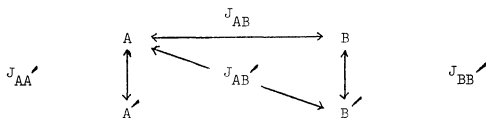


Figure 12. The pmr spectrum of $\text{trans-}[\text{Co}(\text{sdmen})_2(\text{NO}_2)_2]^+$: (A) in 0.01N DCl, (B) in D_2O after several hours (N-deuterated).

complex and mixed complex within. Three of the four mixed complexes with R-pn, give one C-methyl doublet although the methyl groups are not equivalent. The dinitro complexes with S-pn gave two well separated methyl doublets. The $-\text{CH}_2\text{CH}=\text{}$ regions are complex multiplets. The dinitro bis(R-sdmpn) complex exhibits a splitting pattern, resembling those of complexes of R-pn which have been analyzed for ABC splitting patterns and give coupling constants consistent with a gauche chelate ring and an equatorial C-methyl.²⁷

3. PMR spectral analysis

If the diamine chelate rings of trans- $[\text{Co}(\text{sdmen})_2(\text{NO}_2)_2]^+$ are in a symmetrical gauche or an eclipsed conformation, there exist two pairs of equivalent protons: 2-axially and 2-equatorially located protons. These should then exhibit an $\text{AA}'\text{BB}'$ splitting with a coupling scheme:



A spectrum was readily calculated resembling the methylene part of the N-deuterated spectrum of trans- $[\text{Co}(\text{sdmen})_2(\text{NO}_2)_2]^+$ (Figure 13A) if (1) chemical shifts of the A and B protons used were estimated as the midpoints of the two pairs of major peaks, e.g., 152.2 Hz and 183.5 Hz and (2) coupling constants used were those reasonable for a gauche chelate ring,^{30,31} e.g., 4 Hz and 10 Hz for trans and

gauche vicinal coupling constants, respectively, and -12 Hz for geminal coupling constants. An iteration on 17 lines assigned from the experimental spectrum gave a best fit spectrum (Figure 13B) in good agreement with Figure 13A. The parameters obtained were

$$\begin{aligned} J_{AA'} &= 10.7 \text{ Hz} \\ J_{AB} &= -13.1 \text{ Hz} \\ J_{AB'} &= 4.6 \text{ Hz} \\ J_{BB'} &= 4.3 \text{ Hz} \\ \delta_{AB} &= 0.500 \text{ ppm} \end{aligned}$$

The root-mean-square deviation from the 17 assigned lines was 0.083 Hz. The axial and equatorial protons are assigned as the A and B protons, respectively (Figure 14). This is the only assignment that is consistent with $J_{AA'}$ being large and $J_{BB'}$ being small as expected for trans and gauche vicinal coupling constants, respectively. Additional support for this assignment as well as refinement of the calculated spectrum was obtained by using estimated long-range coupling constants between the N-methyl and the ring protons in calculating the spectrum. Estimated coupling constants for A and B with the methyl are 0.5 Hz and 0.1 Hz, respectively. These are determined by measuring the dihedral angle in molecular models between the presumed equatorial methyl group and the axial A and equatorial B protons (ca. 35° and 75°, respectively) and using Barfield's semiempirical coupling constant-dihedral angle relationship,³² developed for methylcycloalkanes, to obtain appropriate coupling constants. Recalculation of the iterated spectrum introducing these coupling constants and, also, the N-methyl

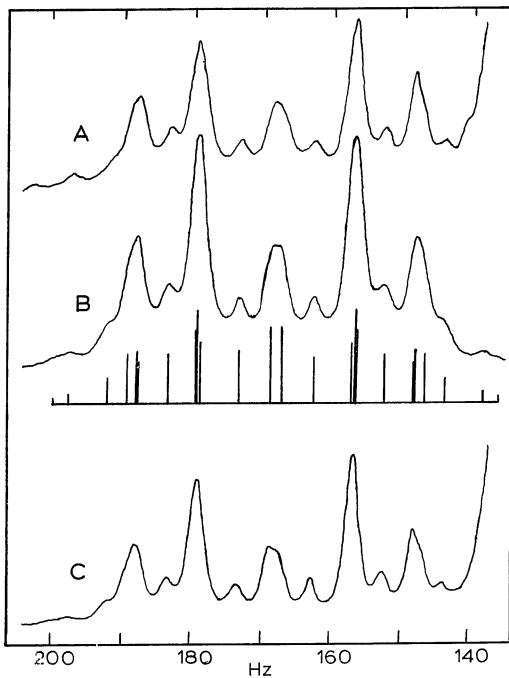


Figure 13. PMR spectra of $\text{trans-}[\text{Co}(\text{sdmen})_2(\text{NO}_2)_2]^+$ in the methylene region: (A) experimental spectrum, (B) calculated AA'BB' spectrum; (C) AA'BB' spectra as in (B) modified with long-range coupling and overlapping methyl peak.

absorption band yield a spectrum (Figure 13C) closely resembling the experimental spectrum. The 100MHz spectral analysis lends additional support to the analysis. The coupling constants obtained were within 0.1 Hz of the 60 MHz results. The similarity of these results indicates that the pmr spectrum in the methylene region can indeed be interpreted as that expected for two equivalent gauche chelate rings with the N-methyl group oriented in an equatorial position.

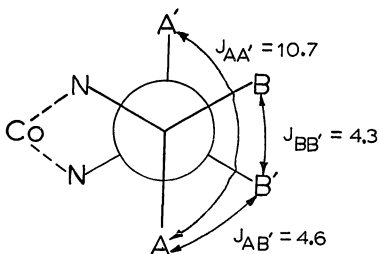


Figure 14. Pmr assignments of methylene protons of $\text{trans-[Co(sdmen)}_2(\text{NO}_2)_2]^+$. Coupling constants are in Hz.

C. Detection of the Dinitro Complexes in Mixtures

When $\text{trans-[Co(en)(sdmen)(NO}_2)_2]^+$ is prepared and isolated, the principle impurities found are $\text{trans-[Co(sdmen)}_2(\text{NO}_2)_2]^+$ and $\text{trans-[Co(en)}_2(\text{NO}_2)_2]^+$, which are easily detected by tlc and pmr analyses. A few percent of the bis(en) complex was easily detected by tlc: this impurity gave a spot with an R_F value of 0.34 (compared to R_F values for the spots from the bis(sdmen) and the mixed(diamine)

complexes of 0.60 and 0.52, respectively). The sensitivity of small amounts of the bis(sdmen) to detection was not as great because it gave a tlc spot close to the major spot of the mixed complex. Pmr analysis was more sensitive to this impurity: it gave a sharp N-methyl peak that was removed from the peaks for the mixed complex, and the intensity of this peak relative to the N-methyl peak of the mixed complex reflected twice the actual concentrations of the bis-(sdmen) impurity. This is because the N-methyl signal arises from four N-methyl groups in the impurity while only two N-methyl groups occur in the mixed complex. Thus, a few percent impurity of the bis complex was readily detected. Once each component was obtained in pure form, mixtures of two of the three components (obtained from column separations) were easily characterized by analyzing uv-visible absorbance measurements taken at two wavelengths at which the behavior of the components were significantly different. The trans-[Co(en)-(R-sdmpn)(NO₂)₂]⁺ ion, obtained by column separation, had trans-[Co(en)₂(NO₂)₂]⁺ and trans-[Co(R-sdmpn)(NO₂)₂]⁺ impurities analogous to those found for trans-[Co(en)(sdmen)(NO₂)₂]⁺, and similar detection techniques were used.

In the isolation of each of the two positional diastereomers of trans-[Co(R-sdmpn)₂(NO₂)₂]⁺, the only impurity detected for each is the other isomer. These impurities could be effectively detected only by pmr analysis. The s-isomer gave a single N-methyl peak for the four N-methyl groups. The f-isomer gave two N-methyl peaks, each arising from two of the four N-methyl groups. One of these signals for the f-isomer occurred at essentially the same chemical

shift as the single s-isomer peak. An impurity of the f-isomer in the s-isomer resulted in a shoulder on the single N-methyl peak of the s-isomer. Since this shoulder arises from two of the four N-methyl, its relative intensity when compared to the main peak, reflects only one half of the actual f-isomer impurity present. Consequently, impurities of a few percent were difficult to detect. Perhaps, this is why Saburi, *et al.*¹⁰ reported only one form (s-isomer) when isolation was done by crystallization. An impurity of the s-isomer in the f-isomer resulted in the low field N-methyl peak being larger than expected.^a Because all of the four methyl groups of the s-isomer contribute to the impurity peak, these deviations in the height of the low field peak of the f-isomer reflects about twice the actual impurity of the s-isomer in the f-isomer.

In the isolation of the two positional diastereomers of trans- $[\text{Co}(\text{R-pn})(\text{R-sdmpn})(\text{NO}_2)_2]^+$ and of trans- $[\text{Co}(\text{S-pn})(\text{R-sdmpn})(\text{NO}_2)_2]^+$ the impurities detected were trans- $[\text{Co}(\text{pn})_2(\text{NO}_2)_2]^+$, trans- $[\text{Co}(\text{R-sdmpn})_2(\text{NO}_2)_2]^+$ and the other isomer of the desired complex. trans- $[\text{Co}(\text{R-sdmpn})_2(\text{NO}_2)_2]^+$ and trans- $[\text{Co}(\text{pn})_2(\text{NO}_2)_2]^+$ were most easily detected by pmr and tlc analyses, respectively. The other isomers were detected by analysis of the pmr spectra in the N-methyl

^aFor this complex and for some of the mixed (diamine) complexes, the N-methyl groups for even the pure complex gave low field peaks that were somewhat more intense than the high field peaks. Presumably, this is because the low field peak overlaps the high field portion of a triplet that is part of the ABC splitting pattern of the CHCH_2 backbone. A similar pattern has been found for complexes of propylenediamine which also have the CHCH_2 backbone.³⁰

region. In each case, both positional diastereomers had two N-methyl peaks: the low field peaks were at essentially the same chemical shift and the high field peaks were separated by about 1.5-2 Hz. Thus, when each isomer was obtained in the pure form, no shoulder from the high field N-methyl peak of the impurity isomer was present, and the intensity of the N-methyl peaks were closer to being equal. As a result, an impurity of the other isomer of a few percent would be undetected.

D. The Stereochemistry of the Complexes of N,N'-Dimethylethylenediamine

1. Characterization of complexes

It is generally acknowledged that the visible and uv-spectra of cobalt(III) diacidobis-(diamine) complexes are characteristic of their geometry. Dinitro complexes with either trans or cis arrangements of the nitro groups are brown. However the trans complexes have the middle absorption band maximum occurring near $28,600\text{ cm}^{-1}$ while for the cis forms, it occurs at about $30,300\text{ cm}^{-1}$. Similarly, dichloro complexes with trans geometry are green, while the cis complexes are violet. The dinitro bis(sdmn) and mixed(sdmn) complexes described here have absorption bands at $28,600\text{ cm}^{-1}$ and $29,000\text{ cm}^{-1}$, respectively, and can be assigned trans geometries. Likewise, both green dichloro complexes have visible and uv-spectra similar to known trans bis-diamine complexes with N-methyldiamines.^{6,10}

The order of elution of the complexes on ion exchange columns and pmr results provide additional support for these assignments.

It has been shown that the elution order on ion-exchange resins can be used as criteria for the identification of geometric isomers of octahedral complexes.³³ In general, trans isomers of diacido-tetramine complexes elute faster than cis isomers. For example, trans- $[\text{Co(en)}_2(\text{NO}_2)_2]^+$ elutes considerably faster on a strong-acid cationic-exchange resin than does the cis isomer. Both the bis and mixed (diamine) dinitro complexes eluted at slightly faster rates than did trans- $[\text{Co(en)}_2(\text{NO}_2)_2]^+$, suggesting that they also have trans geometry. In addition several bands identified as cis isomers eluted at a slower rate. Finally, the pmr spectrum for each of the dinitro and dichloro complexes prepared shows only one type of methyl group. In each case only the trans geometry can give rise to structures with all N-methyl groups in chemically equivalent environments.

The inert asymmetric secondary nitrogen centers of the trans bis(sdmn) complex allows for the existence of seven possible stereoisomers as shown in Figure 15.^a The frequency of the methyl pmr resonance and the splitting pattern of the methylene resonance should both be reasonably sensitive to the structural differences of these possibilities. The optically active form of the dinitro bis(sdmn) complex gave a pmr spectrum indistinguishable from that of the isolated inactive form. This would suggest that the inactive material is composed of only one enantiomeric pair and that the active form is one

^aThe conformations of the diamine chelate rings presented in Figures 1 and 2 are those resulting from equatorial placement of N-methyl substituents and are not necessarily the most stable thermodynamically.

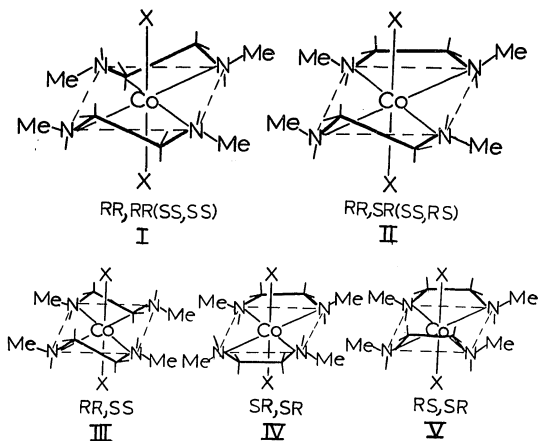


Figure 15. Possible structures of $\text{trans-}[\text{Co}(\text{sdmen})_2\text{X}_2]^+$. Structure I and II exist as a dl form. Structures III-V are meso forms. The designation under each structure is the nitrogen configuration; the designation of each diamine is separated by a comma.

of the enantiomers. If the meso forms and the other possible enantiomeric pairs were present, they were there in such small amounts as to be undetected by pmr. The enantiomeric pair with Structure II^a has 3 asymmetric secondary nitrogen atoms with the same configuration and one with the antipodal configuration, resulting in four non-equivalent methyl groups, which would give a complicated methyl resonance. In contrast, Structure I has all four nitrogen atoms with the same configuration. Assuming that the methyl groups take equatorial positions,^b all four methyl groups would be equivalent and a single methyl resonance would be observed. On this basis the bis(sdmen) complex can be assigned Structure I, Figure 15.

Structure I should also have two types of methylene protons: 4 equivalent axial and 4 equivalent equatorial protons. Structure II should have 8 nonequivalent methylene protons. If Structure I has been assigned correctly to the bis-diamine complex, the methylene resonance of the N-deuterated complex (Figure 13, page 59) should be an AA'BB' multiplet of up to 24 lines, with coupling constants expected for a gauche chelate ring conformation. Structure II, on the other hand, should give rise to a much more complex multiplet. The simplest spectrum expected for Structure II would be due to two

^a In this case and in situations that follow, the term "structure" will be used to denote configurational and conformational designations of metal complexes.

^b Buckingham, et al.,^{2,3} determined the equatorial methyl in complexes of men to be more stable than the axial methyl by $\sim 5 \text{ kcal mol}^{-1}$, using conformational analysis considerations. On similar grounds, Gollogly and Hawkins^{5,4} found the difference to be much smaller ($\sim 1 \text{ kcal mole}^{-1}$). However, Yoshikawa, et al.¹⁰ concluded on the basis of the stereospecific coordination of Nlmpn and N2mpn that the difference should be considerably more than this.

overlapping non-equivalent $AA'BB'$ patterns, one from a gauche chelate ring and the other from either an eclipsed chelate ring shown in Figure 15 or another gauche conformation. The results of the computer analysis performed on the methylene resonance are consistent with only one $AA'BB'$ splitting pattern. The methylene coupling constants obtained are those expected for a gauche conformation (Figure 14, page 60). Furthermore, $J_{AB'}$ and $J_{BB'}$, the two gauche vicinal coupling constants, are nearly equal, consistent with an undistorted gauche conformation. The values of the long-range methyl coupling constants for the axial (0.5 Hz) and equatorial protons (0.1 Hz) are consistent with the methyl group being equatorial to the chelate ring.³² The pmr evidence, then, strongly supports the assignment of Structure I to the dinitro bis(sdmen) complex isolated.

There are three possible stereoisomers for the trans diacido mixed(sdmen) complexes (Figure 16): one meso form and one racemic pair. As was true for the bis(sdmen) case, the pmr spectrum of the active dinitro mixed(sdmen) complex was indistinguishable from that for the inactive material. For the same reasons discussed above, it appears that only the racemic pair was isolated in any detectable amount, which can be assigned Structure I, Figure 16.

Although the methylene resonance of this complex is too complex to be analyzed,^a the similarity of the methyl resonances for the two dinitro complexes suggests that in both complexes, the methyl groups are in similar positions relative to the nitro groups. The

^aTwo non-equivalent overlapping $AA'BB'$ splitting patterns are expected with 48 possible lines for the N-deuterated complex.

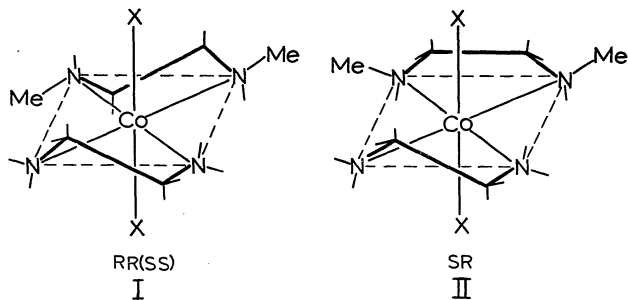


Figure 16. The structure of $\text{trans-}[\text{Co}(\text{en})(\text{sdmen})\text{X}_2]^+$. Structure I exists as a dl form. Structure II is a meso form. The configurational designation of the asymmetric nitrogens are listed below each structure.

sdmen ring conformation in both cases should also be similar. The en ring, on the other hand, should be less restricted and interconvertible from one gauche ring conformation to the other.³⁵ However, the ($\lambda\lambda$) or ($\delta\delta$) ring conformation for the sdmen-en pair is presumably thermodynamically more stable,^a and the predominant conformation is the one determined by the sdmen conformation as shown for Structure I.

The structures of the trans dichloro derivatives can be reasonably assigned as well. Both dichloro complexes must have the same configurations about the asymmetric nitrogen centers as the dinitro complexes because they are converted back to the dinitro complexes from which they were prepared with almost complete retention of activity. The single sharp methyl doublet observed for each dichloro complex supports this assignment.

From the above, it can be concluded that all of the complexes were obtained in only one racemic form, described in Structure I in Figures 15 and 16, in which all of the coordinated secondary amine nitrogen atoms have the same configuration, e.g., either all R or all S. The diamine conformations are determined by the configuration of the asymmetric nitrogen atom. The en conformation is an equilibrium mixture of δ and λ gauche rings, the predominant one having the same chirality as the coordinated sdmen ring.

^aThe energy difference in this case would be expected to be comparable to the 1.2 kcal mole⁻¹ energy difference between the meso and dl trans,trans-[Co(men)₂(NO₂)₂]⁺₂⁺. The meso form has ($\delta\lambda$) and the dl form has ($\delta\delta$) or ($\lambda\lambda$) ring conformations.

2. Conformational considerations and relative isomer stabilities

The existence of only one racemic form for each complex is reasonable in light of approximate conformational stability considerations. The meso isomer of trans,trans- $[\text{Co}(\text{men})_2(\text{NO}_2)_2]^+$ was formed in only 4% yield (compared to the racemic compound) under preparative conditions similar to those used in the present study.³ Conformational analysis studies of models of these two forms are consistent with these results and show that the difference in stability is 0-1 kcal, depending on the number of interactions considered.³ Conformational energy differences between the possible forms of the dinitro complexes under study here appear to be much larger to a first approximation. These differences arise because of significant energy differences between: (1) axial and equatorial placement of the methyl substituent (equatorial placement is more stable by much more than 1 kcal mol⁻¹); (2) eclipsed and gauche chelate ring conformations (gauche conformation of an en ring is more stable by about 5 kcal mol⁻¹);^a and (3) eclipsed and staggered placement of cis methyl groups on different diamines (staggered placement is more stable by more than 10 kcal mol⁻¹).^b The importance of cis methyl-methyl interactions is

^a Gollogly, Hawkins, and Beattie³⁵ have shown recently by conformational analysis that for a isolated ethylenediamine ring, gauche conformations ($\omega \sim 60^\circ$) are more stable than eclipsed conformations ($\omega \sim 0^\circ$) by 4-5 kcal mol⁻¹.

^b Crude calculations from molecular models considering only H-H and C-H interaction between methyl groups estimated from Hill's or Bartell's van der Waals energy curves²⁴ indicate that eclipsed methyl groups are less stable than staggered by considerably more than 10 kcal mole⁻¹.

illustrated by the fact that no trans, cis forms of $[\text{Co}(\text{men})_2(\text{NO}_2)_2]^+$ were reported.⁶

In the structures assigned to the dinitro complexes (Structure I, Figures 15 and 16), all of these interactions are minimized. The other possible racemic bis(sdmen) structure, Structure II (Figure 15), requires that one chelate ring take an eclipsed conformation, and two cis methyl groups be eclipsed. A conformation for II more closely approximating a minimum energy conformation would be to make the eclipsed ring conformation gauche. However, this conformation would require an axial methyl group and the structure should be less stable than I by more than 1 kcal mole⁻¹. The meso forms (III-V) should all be much less stable than I because of at least one of considerations (1) - (3) above. For the dinitro mixed(sdmen) complex, II is less stable than I by about 5 kcal mol⁻¹ because of an eclipsed chelate ring conformation. Making the eclipsed sdmen ring gauche would still make II much less stable than I because of an axial methyl group. From these considerations, it is evident that the other forms of the dinitro complexes should not be obtained in isolable amounts under reaction conditions in which thermodynamic stability is important.

E. The Stereochemistry of the Complexes of (R)-N,N'-Dimethylpropylenediamine, R-sdmpn

1. Conformational considerations and the stereoselective coordination of R-sdmpn

When R-sdmpn coordinates to a metal ion, the two nitrogen centers each may potentially adopt either R or S configurations. Because of

the C-methyl group, the two nitrogen atoms are not equivalent and four possible situations, with regard to the nitrogen centers, exist as shown in Figure 17. The orientation of the C-methyl and N-methyl

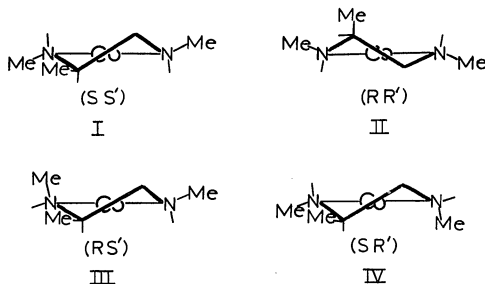


Figure 17. Possible structures of coordinated R-sdmpn. The configurations of the nitrogen centers are shown in parentheses; the configurations of the N_2 methyl substituents are primed.

groups may be either axial or equatorial, depending on the configuration of the C or N and the conformation of the chelate ring. As discussed in the introduction, equatorial methyl groups are favored over axial groups. The drawings in Figure 17 have been constructed with that ring conformation which minimizes the presence of unfavorable axial methyl groups. Structure I is expected to be formed very stereoselectively over Structures II-IV. Structure I allows all of the methyl substituents to be in the more stable equatorial positions.

In Structures III and IV of Figure 17, an N-methyl group is in an axial position, and in Structure II the C-methyl group is in an axial position. From the discussion in Section D concerning the relative stability of an axial and an equatorial N-methyl substituent, it seems reasonable that Structures III and IV are much less favorable than Structure I. However, the degree of instability of Structure II is not as obvious.

Gollogly and Hawkins³⁴ have concluded by conformational analysis studies that the difference in stability between an axial and an equatorial C-methyl group in coordinated propylenediamine is not large as shown by the calculations of Corey and Bailar¹³ but less than 1 kcal mol⁻¹. From these results, it is not expected that Structure I in Figure 17 would be formed stereospecifically with respect to Structure II. It is pertinent to note that in calculating the relative energies of the two conformations of propylenediamine, Gollogly and Hawkins gave the chelate ring with the C-methyl substituent in an axial orientation an unsymmetrical gauche conformation rather than the normal symmetrical gauche conformation (see Figure 18).

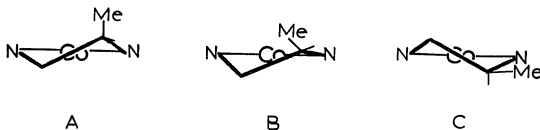


Figure 18. Conformations of (S)-propylenediamine: (A), symmetric λ conformation; (B), unsymmetric λ conformation; (C), symmetric δ conformation.

They determined that for ethylenediamine, conformations A and B are energetically almost equivalent. However, for propylenediamine, conformation B allows much less interaction of the axial C-methyl group with other substituents bonded to cobalt above the chelate ring plane than does conformation A. Consequently, conformation B is much preferred to conformation A and only slightly less preferred to conformation C, which has the C-methyl equatorial.

For R-sdmpn coordinated in Structure II, Figure 17, a similar nonsymmetrical conformation that stabilizes the axial C-methyl group is not possible without simultaneously distorting each N-methyl group from the favorable equatorial position. This is illustrated in Figure 19. On this basis, the preference of Structure I over

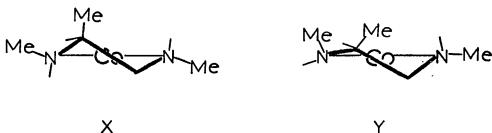


Figure 19. Conformations of coordinated R-sdmpn (R,R'): (X), symmetric δ conformation; (Y), unsymmetric δ conformation.

Structure II (Figure 17) should probably be high, similar to the expected preference of Structure I over Structures III and IV. Thus, it is expected that R-sdmpn will coordinate in a highly stereoselective manner with Structure I, Figure 17.

These conformational considerations also give a firmer rationale to the basis of the stereospecificity that was observed in the

coordination of N_1 and N_2 -methylpropylenediamine. The Japanese workers^{9,10} studying these complexes assumed that the chelate rings with $Nlmpn$ and $N2mpn$ adopt a δ conformation, allowing the C-methyl group to be equatorial. Then, the stereospecificity results because of the relative instability of the axial N-methyl group when the nitrogen atom coordinates with an S configuration (see Figure 20, Structure II). The assumption that the C-methyl group must be

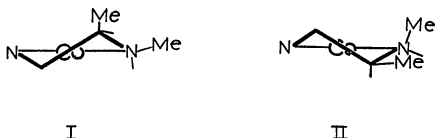


Figure 20. The conformations which result when $Nlmpn$ coordinates with the unfavorable S configuration at the nitrogen center: (I), conformation with an axial C-methyl; (II), S conformation with an axial N-methyl.

equatorial should be made with caution. This follows as a result of the calculations of Gollogly and Hawkins³⁴ which have shown only a small difference in stability between an axial and equatorial C-methyl group in propylenediamine.

However, as found for $R\text{-}sdmpn$, the distortion required to stabilize an axial C-methyl group (Figure 20) in $Nlmpn$ and $N2mpn$ would also distort the N-methyl group from its preferred position. Consequently, the conformation containing an axial C-methyl group would be relatively much more unstable than an equatorial C-methyl group

and stereospecific coordination with S nitrogen configuration would result.

2. Characterization of the complexes

All of the complexes reported here have been assigned as having the acido groups (chloro or nitro) trans. The basis for this assignment has already been discussed in regard to the complexes of sdmen. All of the dinitro complexes that were obtainable in pure form exhibited uv-visible spectra which were similar to those for the analogous trans complexes of sdmen. They had absorption maxima near $28,600\text{ cm}^{-1}$, consistent with trans geometry. These complexes and also the complexes that were not obtained in a pure form (*i.e.*, the mixed complexes with S-pn) eluted on cationic-exchange resin at rates very similar to the trans complexes of sdmen. Pmr evidence could not be given too much weight. Complexes containing coordinated R-sdmpn are expected to give at least two N-methyl signals because of the C-methyl substituent. However, the N-methyl resonances were never different by more than 0.08 ppm which supports the assignment of trans geometry, in which the N-methyl substituent would be in more nearly similar environments than for cis geometry. Finally, the green dichloro complexes prepared here gave uv-visible spectra very similar to the analogous complexes of sdmen. Thus, it appears that the assignment of trans geometry to both dichloro and dinitro complexes of R-sdmpn can be made with confidence.

For the trans bis(R-sdmpn) complex, there are twenty stereoisomers possible (see Table VI): Each nitrogen atom occurs in either an R

TABLE VI

Possible Stereoisomers of trans-[Co(diamine)(R-sdmpn)X₂]⁺

Complex ion	Configuration ^a	Total Isomers ^b
[Co(R-sdmpn) ₂ X ₂] ⁺	(SS')(SS')	2
	(RR')(RR')	2
	(RS')(RS')	2
	(SR')(SR')	2
	(RR')(RS') = (RS')(RR') ^c	2
	(RR')(SS') = (SS')(RR') ^c	2
	(RR')(SR') = (SR')(RR') ^c	2
	(SS')(RS') = (RS')(SS') ^c	2
	(SS')(SR') = (SR')(SS') ^c	2
	(RS')(SR') = (SR')(RS') ^c	2
	Total	20
[Co(R-pn)(R-sdmpn)X ₂] ⁺ or [Co(S-pn)(R-sdmpn)X ₂] ⁺	(SS')	2
	(RR')	2
	(RS')	2
	(SR')	2
	Total	8
[Co(en)(R-sdmpn)X ₂] ⁺	(SS')	1
	(RR')	1
	(RS')	1
	(SR')	1
	Total	4

^aThe configurational designations are for the asymmetric nitrogen atoms. The designations within one parenthesis is for one R-sdmpn. The designation of the N₂ nitrogen atom is distinguished from that of the N₁ nitrogen atom by priming the former. ^bTwo or one stereoisomers when positional diastereomers are or are not possible.

^cThese designations represent the same form.

or S configuration so that each R-sdmpn can coordinate in one of four ways as shown in Figure 17. With two R-sdmpn in the bis complex, there are 4×4 or sixteen possible combinations, which results in ten possible structures (six of the sixteen combinations are repetitions). Each of these ten structures, as a result of the non-symmetrical C-methyl substitution pattern, can exist as a pair of positional diastereomers, accounting for the twenty possible forms.

Only two isomers of the dinitro bis(R-sdmpn) complex were isolated and identified. Each was prepared in significant amounts with the isomer which eluted slower on cationic-exchange resin (s-isomer) the most abundant form. The pmr spectrum of each isomer were similar. The only important distinguishing feature was the N-methyl resonance. The s-isomer exhibited one N-methyl resonance at 2.15 ppm, whereas the fast isomer (f-isomer) exhibited two resonances at 2.12 and 2.16 ppm. The C-methyl doublets and $=CHCH_2-$ multiplets were essentially indistinguishable. Because their pmr spectra are so similar and the yield of each was significant (this presumably reflects only a small difference in their stabilities), the two isomers found for trans- $[Co(R-sdmpn)_2(NO_2)_2]^+$ were assigned the two (SS')(SS') structures shown in Figure 21. These are the positional diastereomers that result from the expected stereoselective coordination of R-sdmpn with S configuration at each asymmetric nitrogen center. It seems reasonable to expect that both positional isomers would be formed in detectable amounts and have similar pmr spectra because major conformational differences between the forms are lacking (e.g., in either form all methyl substituents can be equatorial; chelate ring

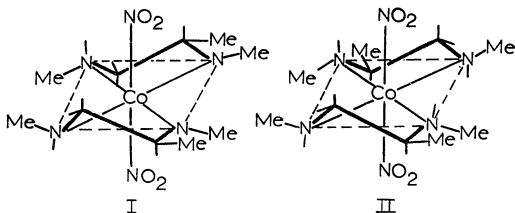


Figure 21. Structures assigned to isomers found for $\text{trans-}[\text{Co}(\text{R-sdmpn})_2(\text{NO}_2)_2]^+$. Each has an S configuration about all nitrogen centers.

pair conformation exist as $(\lambda\lambda)$; and all N-methyl substituents on cis nitrogen atoms can be staggered). Such differences exist between the $(SS')(SS')$ positional isomers and all of the other eighteen possible stereoisomers. The assignment of each positional isomer will be discussed later in this section.

The dichloro complexes which were prepared from the two dinitro stereoisomers are assigned the same structures as found in the dinitro complexes from which they were prepared. The pmr spectra of the dichloro-complexes were distinguishable primarily because of slight difference in the N-methyl region analogous to the dinitro complexes: the s-isomer gave two resonances at 2.35 ppm and 2.38 ppm while the f-isomer gave one resonance at 2.38 ppm.

For the mixed(diamine) complexes with R-pn or with S-pn, there are eight possible stereoisomers (see Table VI). Four different

structures arise because of the four modes of coordination (Figure 17) of R-sdmpn and each of these 4 structures give rise to a pair of positional diastereomers because of the nonsymmetrical methyl substitution on both diamines, accounting for the 8 possible forms. For the mixed complex with ethylenediamine, these positional diastereomers are not possible because ethylenediamine does not have the nonsymmetrical methyl substitution. For this complex, then, there are only four possible structures arising because of the four modes of coordination of R-sdmen (see Table VI).

Two isomers each were found for the dinitro mixed(diamine) complexes with R-pn and with S-pn. Only one isomer was found for the dinitro mixed(diamine) complex with en. As was true for the dinitro bis(diamine) complex, the isomers exhibited similar pmr spectra distinguishable primarily because of the slight differences in the N-methyl resonances. In each case both isomers exhibited two N-methyl resonances. The low field peaks for the isomer pairs were essentially superimposable while the high field peaks exhibited slightly different chemical shifts. (~ 0.05 ppm). Finally, each isomer was prepared in reasonably significant amounts. For the dinitro mixed complex with R-pn, the f-isomer was the most abundant and for the complex of S-pn, the s-isomer appeared to be the major isomer. With this information, it seems logical to assign the structures to the isomer pairs of trans- $[\text{Co}(\text{R-pn})(\text{R-sdmpn})(\text{NO}_2)_2]^+$ and trans- $[\text{Co}(\text{S-pn})(\text{R-sdmpn})(\text{NO}_2)_2]^+$ in a manner analogous to that for trans- $[\text{Co}(\text{R-sdmpn})_2(\text{NO}_2)_2]^+$: the isomer pairs are the positional diastereomers that result if R-sdmpn coordinates in the favored mode with S-configurations about all

nitrogen centers. These are shown in Figure 22. Likewise, the isomer found for trans- $[\text{Co(en)(R-sdmpn)(NO}_2)_2]^+$ is assigned the structure of the one stereoisomer possible that arises from the stereospecific coordination of R-sdmpn with S configurations.

The dichloro complexes that were obtained from the dinitro mixed(diamine) complexes with R-pn exhibited pmr spectra that were distinguishable for each isomer primarily because of small differences of the N-methyl peaks. These complexes were assigned the same structures as the dinitro complexes from which they were prepared, as was the single isomer of the dichloro mixed(diamine) complex of en. The dichloro complex with S-pn was not prepared since the dinitro complexes which were obtained contained impurities of trans- $[\text{Co(R-sdmpn)(NO}_2)_2]^+$.

The conformations of R-sdmpn that are shown in Figure 21 and 22 presumably describe the actual ligand conformations with reasonable accuracy for both the dinitro and dichloro complexes. This is based upon the knowledge that R-sdmpn coordinates in a highly stereoselective manner that is derived from the strong preference of all methyl substituents to take equatorial positions. Secondly, the pmr analysis of the analogous complex of sdmen, trans- $[\text{Co(sdmen)}_2(\text{NO}_2)_2]^+$, gave coupling constants consistent with normal gauche ring conformations and N-methyl substituents in equatorial positions. The conformations of the other diamine (e.g., R-pn, S-pn or en) are assigned on different grounds. The conformations of R-pn and en are assigned as being λ as shown in Figure 22. This is the same as the conformation of the R-sdmpn ring. The basis for this assignment is the same as discussed in section C for the mixed complex of sdmen

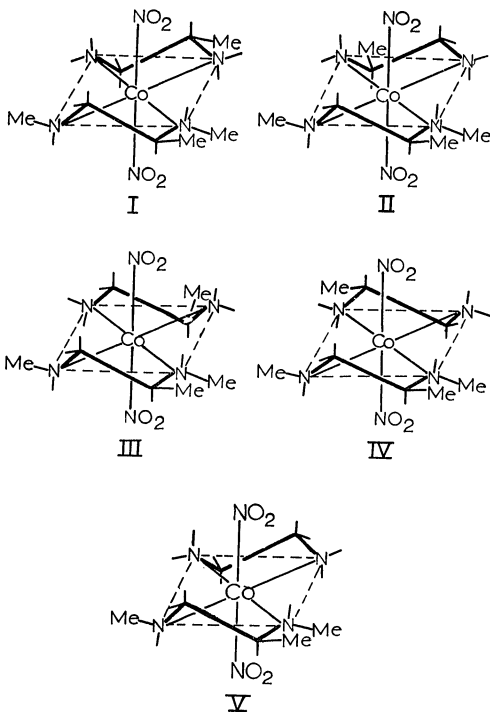


Figure 22. Stereoisomer assignments for the dinitro mixed(diamine) complexes of R-sdmpn. Structures I, II, and III, IV are cis and trans positional diastereomers of trans- $[\text{Co}(\text{R-pn})(\text{R-sdmpn})(\text{NO}_2)_2]^+$ and trans- $[\text{Co}(\text{S-pn})(\text{R-sdmpn})(\text{NO}_2)_2]^+$, respectively. Structure V is the only possible form of trans- $[\text{Co}(\text{en})(\text{R-sdmpn})(\text{NO}_2)_2]^+$.

with en: The R-sdmpn-en and R-sdmpn-R-pn ring pair conformation is more stable as $(\lambda\lambda)$ than as $(\lambda\delta)$ because of diamine-diamine interaction. In addition, for the complex with R-pn, the C-methyl substituent reinforces this conformational preference because of the tendency of the methyl group to be in the equatorial position allowable when R-pn takes a λ conformation.

The conformational assignment of S-pn in the mixed complex with R-sdmpn is not as straight forward as for the other two mixed complexes with en and R-pn. The assignment of a δ conformation as shown for Structures III and IV in Figure 22 is based upon the knowledge that the C-methyl group on S-pn prefers an equatorial position, and this requires that the conformation be δ . However, this results in the (R-sdmpn)-(S-pn) ring pair having a $(\lambda\delta)$ ring pair conformation which should be less stable than $(\lambda\lambda)$. If the ring pair conformation was $(\lambda\lambda)$, this would result in the C-methyl group on R-pn being axial.

Pmr evidence supports the $(\lambda\delta)$ conformational assignment shown in Structures III and IV, Figure 22. Dabrowiak and Cooke³⁷ have pointed out that steric compression effects on pmr spectra can be used for assigning the conformations of chelate rings. For example, the meso form of trans,trans- $[\text{Co}(\text{men})_2\text{X}_2]^+$ has a $(\delta\lambda)$ conformation while the dl form as a $(\delta\delta)$ and $(\lambda\lambda)$ conformation. The environment at the N-methyl group is different in each complex because of the difference in conformation (see Figure 23). The N-methyl group in the meso form is eclipsed by an amine hydrogen atom of the other chelate ring. In the dl form, the N-methyl group is staggered with

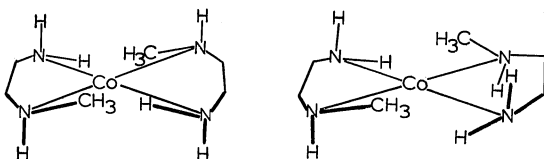


Figure 23. Conformations of isomers of $\text{trans,trans-}[\text{Co}(\text{men})_2\text{X}_2]^+$ showing the different environment of each N-methyl: (I) meso form; (II) levo form.

respect to the two amine hydrogen atoms on the other chelate ring. The increased van der Waals interactions between the N-methyl groups and the amine hydrogen atoms in the meso form (referred to as steric compression) results in the N-methyl protons being deshielded as compared to the analogous protons in the dl form. In the dinitro complex, the pmr resonance of the N-methyl group in the meso form is downfield from the resonance for the dl form by 0.11 ppm (2.34 ppm vs 2.23 ppm). A similar trend is observed for the dichloro and chloronitro analogs. If the stereoisomers found for $\text{trans-}[\text{Co}(\text{S-pn})(\text{R-sdmpn})(\text{NO}_2)_2]^+$ have $(\delta\lambda)$ ring pair conformations (S-pn has a δ conformation), the N-methyl resonances should on the average be downfield of those found for $\text{trans-}[\text{Co}(\text{R-pn})(\text{R-sdmpn})(\text{NO}_2)_2]^+$ (assigned a $(\lambda\lambda)$ conformation) by about 0.11 ppm. This is because the N-methyl group in the former should be deshielded by steric compression relative to the latter in the same way as was found for the isomers of $\text{trans,trans-}[\text{Co}(\text{men})_2(\text{NO}_2)_2]^+$. If the $(\lambda\lambda)$ conformation is predominantly present, then no such shift should be observed. If a rapid equilibrium of significant amounts of each conformation is

present, then the shift should be less than 0.11 ppm. From Table V, it can be seen that the N-methyl peaks occur at an average value of 2.34 ppm (2.29-2.37 ppm) for the dinitro complex of S-pn and at an average value of 2.22 ppm (2.19-2.25) for the complex of R-pn. From these results it can be concluded that trans- $[\text{Co}(\text{S-pn})(\text{R-sdmpn})(\text{NO}_2)_2]^+$ and the dichloro analogs have a λ conformation for the R-sdmpn ring and a δ conformation for the S-pn ring.

At this point, it can easily be rationalized why the mixed complex with S-pn was prepared in such small yields when compared to the other mixed complexes: the favored products are the bis(R-sdmpn) and bis(S-pn) complexes because they can take the more favored ($\lambda\lambda$) and ($\delta\delta$) conformations, respectively, and keep all methyl substituents in equatorial positions.

3. Assignment of positional diastereomers

Only one other case is known where positional diastereomers, arising from C-methyl substitution, have been found for trans-diacidobis(diamine) type complexes. Hawkins, et al.³⁸ showed that two forms existed for trans- $[\text{Co}(\text{R-pn})_2\text{Ch}]^+$. These were detected by tlc with one spot being more abundant than the other. Saito, et al.¹² determined from an X-ray analysis of presumably the major isomer that it was the positional diastereomer with the C-methyl substituents located adjacent to trans nitrogen atoms (trans,trans isomer rather than trans,cis isomer). The positional diastereomers found here for trans- $[\text{Co}(\text{R-sdmpn})_2(\text{NO}_2)_2]^+$, trans- $[\text{Co}(\text{R-pn})(\text{R-sdmpn})(\text{NO}_2)_2]^+$ and trans- $[\text{Co}(\text{S-pn})(\text{R-sdmpn})(\text{NO}_2)_2]^+$ occurred with one isomer being more

abundant than the other by about 2:1.

Because the major form of $\text{trans-}[\text{Co}(\text{R-pn})\text{Cl}_2]^+$ was found to be the trans,trans isomer, the major forms of $\text{trans-}[\text{Co}(\text{R-sdmpn})_2(\text{NO}_2)_2]^+$ (s-isomer) trans-}[\text{Co}(\text{R-pn})(\text{R-sdmpn})(\text{NO}_2)]^+ (f-isomer), and trans-}[\text{Co}(\text{S-pn})(\text{R-sdmpn})(\text{NO}_2)_2]^+ (s-isomer) can be assigned the trans,trans structures shown as Structures II in Figure 21 and II and IV in Figure 22. Other criteria that could be used for assigning the isomer pairs are relative column elution rates and differences in the pmr spectra. At the present time, the basis for using pmr does not seem sound enough for assignment. On the other hand, elution rates as a criterion does not seem valid: for two of the complexes, the s-isomer was more abundant while for the other complex the f-isomer is the more abundant. (One would expect one geometry to elute the fastest for all cases.)

F. Assignment of the Absolute Configuration to the Complexes

All of the complexes containing (R)-N,N'-dimethylpropylene-diamine can be assigned S configurations around the secondary nitrogen centers and λ chiralities of the chelate rings formed by R-sdmpn. The absolute configuration of the free amine and the chelated amine are summarized in Figure 24. These assignments are readily deduced from the treatment of the stereoselectivity in Section D: the C-methyl group on the asymmetric carbon atom of R configuration imposes a λ conformation by taking the favored equatorial position and thus, both secondary amines must coordinate with an S configuration so that the N-methyl substituents can take the favored

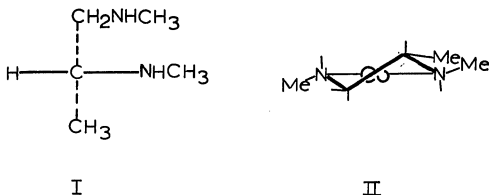


Figure 24. The absolute configuration of (I) R-sdmnp and (II) chelated R-sdmnp in most stable form.

equatorial positions as well. In the mixed complexes, the chelate rings of en and R-pn take a λ conformation, also, but the chelate rings of S-pn take a δ conformation (the reasons have already been discussed in Section D).

In the remainder of this section, the absolute configurations will be assigned by methods which will relate the absolute configuration of the complexes to the chirality of the optical activity of d-d metal transitions. This is a method which is commonly used to assign absolute configurations.³⁹ The sign of CD bands corresponding to d-d metal transitions of $A_{1g} \rightarrow T_{1g} (O_h)$ parentage will be correlated with the absolute configuration. In tetragonally distorted complexes, (all trans diacidotetramine are of this type) the $A_{1g} \rightarrow T_{1g}$ transition will become two transitions in the lower symmetry field (see Figure 25) because of the splitting of the excited state. For the dinitro complexes, this splitting is not very evident

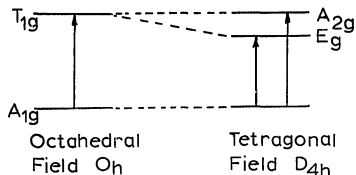


Figure 25. Tetragonal splitting of excited states of Co(III) that results in two transitions from the $A_{1g} \rightarrow T_{1g}$ transition.

from the CD curve. For the dichloro complexes, there are two almost completely separated bands. In some dichloro complexes, there is even evidence of a small amount of splitting of the $A_{1g} \rightarrow E_g$ transition, suggesting that the symmetry is somewhat lower than D_{4h} .

With this background, the absolute configuration of the dichloro complexes of N,N' -dimethylethylenediamine can be deduced from a treatment similar to that which Saburi, *et al.*⁹ used to assign the correct absolute configuration of $(-)_D$ -trans,trans- $[\text{Co}(\text{men})_2\text{Cl}_2]^+$. They based their assignment on a comparison of the CD curves in the $A_{1g} \rightarrow T_{1g}$ region (15 - $23,000 \text{ cm}^{-1}$) for the levo complex of men with those for trans- $[\text{Co}(\text{NLmpn})_2\text{Cl}_2]^+$ and the analogous N2mpn complex (this has been discussed in detail in the introduction). The latter two complexes were known to have δ chelate ring chiralities and an R configuration about the secondary amine nitrogen atoms. The similarities in the CD curves between these two complexes and the levo complex of men led these workers to assign δ ring chiralities and

an R configuration about the nitrogen atoms for the levo men complex. These assignments seemed reasonable because the structures of the three complexes are very comparable. The only difference is that the complexes of N1mpn or N2mpn has an equatorial C-methyl group on each ring whereas the complex of men does not.

On similar grounds, the absolute configuration of $(+)_{\text{D}}\text{-trans-}[\text{Co}(\text{sdmen})_2\text{Cl}_2]^+$ can be deduced from a comparison of its CD curve to that for trans- $[\text{Co}(\text{R-sdmpn})_2\text{Cl}_2]^+$. These complexes, which differ in structure by only an equatorial methyl substituent, have very similar CD curves in the $A_{1g} \rightarrow T_{1g}$ region (see Figures 9 and 11, pages 46 and 49). The complex of R-sdmpn has an S configuration around the secondary nitrogen centers and a λ conformation of the chelate ring. Then, $(+)_{\text{D}}\text{-trans-}[\text{Co}(\text{sdmen})_2\text{Cl}_2]^+$ must also be assigned this absolute configuration. It follows that the configuration of $(+)_{\text{D}}\text{-trans-}[\text{Co}(\text{en})(\text{sdmen})\text{Cl}_2]^+$ can be deduced by comparing its CD curve to that for trans- $[\text{Co}(\text{en})(\text{R-sdmpn})\text{Cl}_2]^+$. The CD curves of these complexes closely resemble each other, and the configurations about the secondary nitrogen atoms and the ring chiralities in the mixed complex of sdmen must be assigned S and λ , respectively, as in the mixed complex of R-sdmpn.

The absolute configurations of the analogous dinitro complexes of sdmen can also be assigned. One method is to assign them the same configurations as the dichloro complexes which were prepared from them. In this way, $(-)_{\text{D}}\text{-trans-}[\text{Co}(\text{sdmen})_2(\text{NO}_2)_2]^+$ and $(-)_{\text{D}}\text{-trans-}[\text{Co}(\text{en})(\text{sdmpn})(\text{NO}_2)_2]^+$, which both convert to the analogous levo dichloro complexes, are assigned λ ring chiralities and S secondary

nitrogen configurations. Another method of assignment for the dinitro complexes of sdmen is analogous to that used for the dichloro complexes. In the $A_{1g} \rightarrow T_{1g}$ region, these dinitro N-methyl substituted diamine complexes exhibit only one significant band (near $22,000 \text{ cm}^{-1}$). This band is negative for $(-)_D\text{-trans-}[\text{Co}(\text{sdmen})_2(\text{NO}_2)_2]^+$ and $\text{trans-}[\text{Co}(\text{R-sdmpn})_2(\text{NO}_2)_2]^+$, (Figure 8 and 10, pages 45 and 48) resulting in assigning to the former complex λ ring chiralities and an S configuration around the secondary nitrogen atoms. Likewise, this band for $\text{trans-}[\text{Co}(\text{en})(\text{sdmen})(\text{NO}_2)_2]^+$ and $\text{trans-}[\text{Co}(\text{en})(\text{R-sdmpn})(\text{NO}_2)_2]^+$ is negative, suggesting λ and S configurational assignments. It can be seen that the two approaches used with the dinitro complexes give consistent assignments.

There is a more general approach to making the absolute configurational assignments to $\text{trans-diacidotetramine cobalt(III)}$ complexes. It has been shown recently for a series of $\text{trans-dichloro-tetramine cobalt(III)}$ complexes of N-methyl and C-methyl substituted ethylenediamines^{10,17} and triethylenetetramines³⁶ that the sign of the CD band near $22,000 \text{ cm}^{-1}$ ($A_{1g} \rightarrow A_{2g}$ component) can be related to the configuration around the asymmetric nitrogen centers. This apparently applies in cases where the methyl substituents are on adjacent or on opposite nitrogens. For example, $\text{trans-}[\text{Co}(\text{L-1,3,8,10-Metrien})\text{Cl}_2]^+$, a complex of a linear tetramine which has two N-methyl substituents on adjacent nitrogen atoms, and $\text{trans,trans-}[\text{Co}(\text{Nlmpn})_2\text{Cl}_2]^+$, which has the N-methyl groups on opposite nitrogen atoms, are known to have R configurations around the N-methyl nitrogen centers and negative CD bands at $22,000 \text{ cm}^{-1}$. Using this approach for the dichloro

complexes studied here as well as for the dinitro complexes, the sign of the major peaks at $22,000\text{ cm}^{-1}$ implies assignments consistent with those determined in the preceding paragraphs.

Apparently, for the CD transition near $22,000\text{ cm}^{-1}$, the major part of the optical activity is derived from the N-methyl asymmetric nitrogen atoms, and this more general approach can be used. In spite of variations of the structure of the trans-diacidotetramine complexes being considered, the sign of the CD band does not change if the configurations of the asymmetric nitrogen atoms do not change.

G. Circular Dichroism and the Hexadecadal Rule

The work of Shellman¹⁹ and Mason¹⁸ on the development of a regional sign rule to describe circular dichroism has already been discussed in the introduction. Following the symmetry arguments of Shellman, Mason has suggested that the optical activity of the metal d-d transitions (for cobalt(III), this would be the $A_{1g} \rightarrow T_{1g}(O_h)$ transitions which are the only ones allowed in terms of optical activity) of dissymmetric trans-diacidotetramine type complexes can be interpreted with a regional signed rule. This optical activity can be discussed in a more detailed manner than attempted in the last section (*i.e.*, determination of the absolute configurations of the asymmetric nitrogen atoms). Using the hexadecadal rule of Mason, the activity for this type of complex is proposed to arise from additive perturbing effects from amine substituents which are situated out of the tetragonal amine nitrogen atom plane and which lower the tetragonal symmetry. Accordingly, the regions of space above and

below this plane can each be divided into octants in a nodal manner. The sign of each octant depicts the contribution to the activity of a perturbing substituent in that octant. For example, the regional sign relationship is shown in Figure 26 for $(+)\text{D-trans-}[\text{Co}(\text{sdmpn})_2\text{Cl}_2]^+$, $(+)\text{D-trans-}[\text{Co}(\text{en})(\text{sdmen})\text{Cl}_2]^+$ and $(+)\text{D-trans,trans-}[\text{Co}(\text{men})_2\text{Cl}_2]^+$.

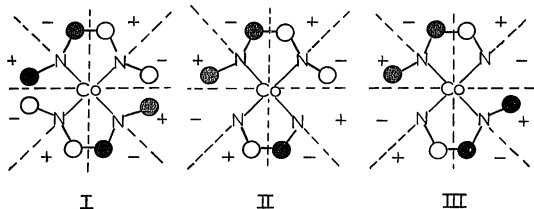


Figure 26. The regional sign arrangement above the Co-N_4 plane of contributions by diamine moieties to the $A_{1g} \rightarrow A_{2g}(D_{4h})$ CD bands in (I) $(+)\text{D-trans-}[\text{Co}(\text{sdmen})_2\text{Cl}_2]^+$, (II) $(+)\text{D-trans-}[\text{Co}(\text{en})(\text{sdmen})\text{Cl}_2]^+$, and (III) $(+)\text{D-trans,trans-}[\text{Co}(\text{men})_2\text{Cl}_2]^+$. Carbon atoms above the plane ($+\underline{Z}$) are represented as solid circles (•) and below ($-\underline{Z}$) as open circles (○). The signs shown are for substituent contributions in $+\underline{Z}$ space while those in $-\underline{Z}$ are of opposite sign.

The signs shown indicate the contribution expected to the $A_{1g} \rightarrow A_{2g}(D_{4h})$ CD band of a substituent in the $+\underline{Z}$ direction. Those in the $-\underline{Z}$ direction are of opposite sign. The corresponding contributions expected for the $A_{1g} \rightarrow E_g(D_{4h})$ CD band are of opposite sign to those for the $A_{1g} \rightarrow A_{2g}(D_{4h})$ CD band. The solid circles in Figure 26 represent carbons in $+\underline{Z}$ space and open circles represent carbons in $-\underline{Z}$ space. It can be seen that for $(+)\text{D-trans-}[\text{Co}(\text{sdmen})_2\text{Cl}_2]^+$, there are four N-CH_3 substituents which should contribute positively and four CH_2 groups (from two chelate rings) which should contribute

negatively to the $A_{1g} \rightarrow A_{2g}$ CD band. In the other two dextro complexes, there are two $N-CH_3$ groups each which should contribute positively. The observed CD peaks for these complexes should represent the additive contributions of these various groups.

1. The dichloro complexes and the validity of the hexadecadal rule in the $A_{1g} \rightarrow A_{2g}$ CD region

For the dichloro complexes, the $A_{1g} \rightarrow T_{1g}(O_h)$ d-d transition splits into two tetragonal components, the $A_{1g} \rightarrow A_{2g}$ component (the CD band is near $21,000\text{ cm}^{-1}$) and the $A_{1g} \rightarrow E_g$ component (the CD band is near $15,000\text{ cm}^{-1}$), and these components are widely separated (see section F and Figure 25). The CD band corresponding to the $A_{1g} \rightarrow A_{2g}$ component always appears as a simple band which is unaffected by overlap with neighboring bands. This is not true for the CD region corresponding to the $A_{1g} \rightarrow E_g$ component, which may be split as the symmetry deviates from D_{4h} . Thus, an examination of variations in the CD band intensity (the CD band height at the maxima) for the isolated $A_{1g} \rightarrow A_{2g}$ CD band for a series of trans-diacidobis(diamine) cobalt(III) complexes in which the stereochemistry is reasonably well characterized and in which the position, number, and type of perturbing substituents are varied, would seem to give the hexadecadal rule a fair test. This CD band is ideal for this study because it appears to be unaffected by overlap with neighboring bands.

A reasonable approach to use in determining the magnitude of the substituent contributions from an $N-CH_3$ group and from a CH_2 to the CD intensity is as follows. The $A_{1g} \rightarrow A_{2g}$ CD band intensity

for trans- $[\text{Co}(\text{R-pn})_2\text{Cl}_2]^+$ is -0.11 .⁴⁰ Contributions to this intensity come from two CH_2 groups and two CHCH_3 groups of the two λ chelate rings. A comparison of this value to the analogous value for trans- $[\text{Co}(\text{R-chxn})_2\text{Cl}_2]^+$ (-0.07)⁴¹, where the chelate ring is the same conformation but where additional equatorial C-alkyl substitution has been added, suggests that the C-methyl substituent in chelated R-pn has only a minor contribution to the activity. The main contribution is from the puckered ring as suggested by Hawkins.¹⁷ The small vicinal effect for R-pn in complexes of cobalt(III) with ethylenediamine-diacetic acid type ligands (-0.01 to -0.03)^{42,43} and the small variations in the $A_{1g} \rightarrow A_{2g}$ CD band intensity for trans- $[\text{Rh}(\text{diamine})_2\text{Cl}_2]^+$ complexes of R-pn (0.12) and 2,3-butanediamine (0.11) supports this.⁴⁴ Because the band intensities change little as equatorial alkyl substituents are varied on ethylenediamine chelate rings, it seems reasonable to assume that to a first approximation, the value, -0.11 , is the CD intensity from four CH_2 groups in two λ chelate rings (i.e., the CHCH_3 are assumed to contribute the same as CH_2 groups). Then, the contribution of four N- CH_3 groups can be determined by subtracting the ring contribution (0.11) from trans- $[\text{Co}(\text{R-pn})_2\text{Cl}_2]^+$ from the CD band intensity for $(+)_D$ -trans- $[\text{Co}(\text{sdmen})_2\text{Cl}_2]^+$ (1.42) to give 1.53 or 0.38 for each N- CH_3 . The CD intensity for this sdmen complex is probably a good choice to be used for determining a representative N- CH_3 contribution. From pmr results of the dinitro analog, it would be expected that the dichloro complex has a normal gauche diamine conformation with N- CH_3 groups in undistorted equatorial positions. Also, the band intensity for this complex results more

from the N-CH_3 contribution than for other complexes with two N-CH_3 groups, and using it should introduce less relative error from the assumed CH_2 contribution.

With 0.38 as the contribution of the N-CH_3 (nitrogen with an S-configuration) and -0.11 as that of four CH_2 groups (from two λ chelate rings), the $A_{1g} \rightarrow A_{2g}$ CD intensities can be calculated for the other two complexes in Figure 25. Also, assuming the CH_2 to be equivalent to CHCH_3 , the expected CD intensities for the bis-(R-Nlmpn) and bis(R-N2mpn) complexes^a (they would fit Structure III, Figure 25); the bis(R-sdmpn) complexes (they would fit Structure I, Figure 25); and the mixed complexes of R-sdmpn with R-pn (they would fit Structure II, Figure 25) can be calculated. The results are shown in Table VIII.

The results seem to indicate general agreement between expected and measured values. All of the complexes with two N-CH_3 groups (E-J, Table VII) have band intensities in the range, 0.51 to 0.77; the complexes with four N-CH_3 groups (B-D) have intensities in the range of 1.42 to 1.62. In spite of these small deviations, which are not unreasonable, the results strongly suggest the validity of a hexadecadal rule in predicting the N-CH_3 substituent effects on the $A_{1g} \rightarrow A_{2g}$ CD band activity. The contribution of four N-CH_3 substituents is essentially twice that for two. The contribution of

^aIn this work complexes were prepared and studied that have S configurations at the nitrogen centers and λ chelate rings of the N,N - dimethyl substituted diamines. In order for the other complexes to conform to this, the R-Nlmpn and R-N2mpn complexes and the (+)_D-trans,trans-[Co(men)₂Cl₂]⁺ ion, which are enantiomeric to those prepared, are discussed.

TABLE VII

Calculated CD Intensities of the $A_{1g} \rightarrow A_{2g}(D_{4h})$ CD band for the Dichloro Complexes

	Complex Ion	Expected Contribution	CD Intensities	
			Calculated	Observed
A	<u>trans</u> - $[\text{Co}(\text{R-pn})_2\text{Cl}_2]^+$	4 CH_2^b	0.11	0.11 ^a
B (+) _D	<u>trans</u> - $[\text{Co}(\text{sdmen})_2\text{Cl}_2]^+$	4 N-CH ₃ , 4 CH_2	1.42	1.42 ^a
C	<u>trans</u> - $[\text{Co}(\text{R-sdmpn})_2\text{Cl}_2]^+$ s-isomer	4 N-CH ₃ , 4 CH_2^b	1.42	1.59
D	f-isomer		1.42	1.62
E (+) _D	<u>trans</u> - $[\text{Co}(\text{en})(\text{sdmen})\text{Cl}_2]^+$	2 N-CH ₃ , 4 CH_2	0.65	0.52
F	<u>trans</u> - $[\text{Co}(\text{en})(\text{R-sdmpn})\text{Cl}_2]^+$	2 N-CH ₃ , 4 CH_2^b	0.65	0.59
G	<u>trans</u> - $[\text{Co}(\text{R-pn})(\text{R-sdmpn})\text{Cl}_2]^+$ s-isomer	2 N-CH ₃ , 4 CH_2^b	0.65	0.62
H	f-isomer		0.65	0.63
I (+) _D	<u>trans,trans</u> - $[\text{Co}(\text{men})_2\text{Cl}_2]^+$	2 N-CH ₃ , 4 CH_2	0.65	0.62
J	<u>trans,trans</u> - $[\text{Co}(\text{R-Nlmpn})_2\text{Cl}_2]^+$	2 N-CH ₃ , 4 CH_2^b	0.65	0.77
K	<u>trans,trans</u> - $[\text{Co}(\text{R-N2mpn})_2\text{Cl}_2]^+$	2 N-CH ₃ , 4 CH_2^b	0.65	0.51

^aThese values used to calculate contributions used.
the contribution for CHCH_3 is the same as for CH_2 .

^bAssuming that

two cis N-CH₃ substituents in Structure II, Figure 25 (E-H, 0.52 to 0.63) is essentially the same as two trans N-CH₃ substituents in Structure III (I-K, 0.51 to 0.77). This is predicted by the hexadecadal rule because with either Structure II or III, both N-CH₃ substituents lie in positive regions of space.

The (+)_D-trans-[Co(en)(sdmen)Cl₂]⁺ and (+)_D-trans,trans-[Co(men)₂Cl₂]⁺ ions have CD intensities which are somewhat lower than expected. These complexes were converted back to the dinitro complexes with 84% and 90% optical purity, respectively. These losses in optical purity presumably result from racemizations which may have occurred during the preparation of the dichloro complexes (carried out in concentrated HCl); but also, they may have occurred in the conversion back to the dinitro compounds (carried out in more dilute acid, 0.01 M HClO₄). Thus, the possibility exists that the band intensities reported are not those of the optically pure complexes. The corrected values would give better agreement with expected values. However, racemization is base catalyzed, and it is more likely that racemization did not occur in the preparation of the dichloro complexes because of the concentrated acid conditions. This conclusion is supported by the fact that the mixed dichloro complex prepared at either 53° or 70° was converted back to dinitro complex of the same activity. If the loss of activity occurred during the preparation of the dichloro complex, different results would have been expected at the different temperatures.

Other small deviations that exist between calculated and measured CD intensities appear to occur because C-CH₃ substituents do contribute

measurably to the activity (it was assumed that they do not). For example, if one examines the results of the mixed(diamine) complexes (E-H), a very small effect (0.03 to 0.04) is observed for C-CH₃ groups on the diamine with no N-methyl substitution (e.g., compare trans-[Co(R-pn)(R-sdmpn)Cl₂]⁺ (0.63, 0.62) to trans-[Co(en)(R-sdmpn)Cl₂]⁺ (0.59)). A larger effect (0.07) is observed for C-CH₃ substituents on the diamine with N-CH₃ substitution (e.g., compare trans-[Co(en)(R-sdmpn)Cl₂]⁺ (0.59) and trans-[Co(R-pn)(R-sdmpn)Cl₂]⁺ (0.63, 0.62) to (+)_D-trans-[Co(en)(sdmen)Cl₂]⁺ (0.52). An analogous effect for two C-CH₃ (0.08 to 0.10 per C-CH₃) is observed for the bis complexes prepared here (e.g., compare trans-[Co(R-sdmpn)₂Cl₂]⁺ (1.59, 1.62) to (+)_D-trans-[Co(sdmen)Cl₂]⁺ (1.42)). Examination of molecular models for these complexes suggests that interactions between N-CH₃ and C-CH₃ in R-sdmpn could be important because the methyls are on adjacent atoms and are in close proximity of each other. Such interactions could result in a small distortion of the gauche conformation of R-sdmpn which would move both the C-CH₃ and N-CH₃ slightly from their normally preferred equatorial positions as depicted in Figure 27. This would yield a somewhat larger CD contribution from the N-CH₃ than normally expected because it lies further above the tetragonal plane. The change in the C-CH₃ contribution should be small in comparison because it lies close to the tetragonal plane and is small initially. An analogous interaction as this could also explain the fact that the A_{1g} → A_{2g} CD band for trans,trans-[Co(N2mpn)Cl₂]⁺ (0.77), which has two C-CH₃ adjacent to two N-CH₃ groups, is 0.15 larger (or 0.08 per distorted N-CH₃) than

(+)_D-trans,trans-[Co(men)₂Cl₂]⁺.

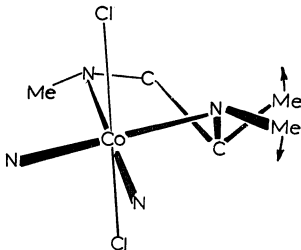


Figure 27. Possible distortion of coordinated R-sdmpn. The arrows represent the direction of the distortion of the methyl conformations.

In the bis N2mpn and the mixed en-sdmen complexes, the CD values are somewhat less than expected when compared to the bis(men) complexes (0.51 and 0.52 vs 0.62). In these complexes, there exists a second methyl group (either C- or N-methyl) on the same chelate ring as an N-methyl (but not adjacent to it so that the distortion in N1mpn does not occur). Apparently, the presence of this second group results in an additional distortion of the chelate ring, allowing each group to be more equatorial (and thus give a smaller CD contribution) than expected.

In the bis(sdmen) complex this effect would not occur as further equatorial distortion of the N-methyl groups would increase repulsions between N-methyl groups on neighboring chelate rings.

2. The dichloro complexes and the validity of the hexadecadal rule in the $A_{1g} \rightarrow E_g$ CD region

For the dichloro complexes, the $A_{1g} \rightarrow E_g$ CD region (near 15,000 cm^{-1}) should also lend itself to interpretation by a hexadecadal rule. However, this region is more complicated than the $A_{1g} \rightarrow A_{2g}$ region. As can be seen from Figures 9 and 11, section VB, in some complexes, the $A_{1g} \rightarrow E_g$ band splits into two bands with a splitting which is very small compared to the splitting between the $A_{1g} \rightarrow A_{2g}$ and $A_{1g} \rightarrow E_g$ components. When this occurs, the major CD component of this $A_{1g} \rightarrow E_g$ band is usually at lower energy than the minor component and of the same sign as the unsplit $A_{1g} \rightarrow E_g$ CD band in other complexes. It has been proposed that for the complexes of men ,⁶ Nlmpn ¹⁰ and N2mpn ¹⁰, the $A_{1g} \rightarrow E_g(D_{4h})$ transition splits into two components of opposite signs ($A \rightarrow A$ and $A \rightarrow B$) because of lower than D_{4h} symmetry. The CD spectrum that results from the overlap of these two CD bands of opposite sign would be expected to be not as reliable for analysis of the hexadecadal rule for spectrum in the $A_{1g} \rightarrow A_{2g}$ region. Nevertheless, the $A_{1g} \rightarrow E_g$ CD band (or the low energy component when two components exist) will be treated as in the previous section for the $A_{1g} \rightarrow A_{2g}$ CD band.

The band intensity of trans- $[\text{Co}(\text{R-pn})\text{Cl}_2]^+$ (0.71)⁴⁰ in this region is assumed to be the contribution of four CH_2 groups in two λ chelate rings on the same grounds as discussed earlier for the $A_{1g} \rightarrow A_{2g}$ CD band. Experimental evidence supports this assumption.^{41,44} Then, by subtracting this intensity from that for (+)_D-trans- $[\text{Co}(\text{sdmen})_2\text{Cl}_2]^+$ (1.07), the contribution for one N-CH_3 would be -0.44.

TABLE VIII

Calculated CD Intensities of the $A_{1g} \rightarrow E_g(D_{4h})$ CD
band for the Dichloro Complexes

	Complex Ion	Expected Contribution	CD Intensities	
			Calculated	Observed
A	<u>trans</u> -[Co(R-pn) ₂ Cl ₂] ⁺	4 CH ₂ ^b	-0.71	-0.71 ^a
B	(+) _D - <u>trans</u> -[Co(sdmn) ₂ Cl ₂] ⁺	4 N-CH ₃ , 4 CH ₂	-1.07	-1.07 ^a
C	<u>trans</u> -[Co(R-sdmpn) ₂ Cl ₂] ⁺ s-isomer	4 N-CH ₃ , 4 CH ₂ ^b	-1.07	-2.42
D	f-isomer		-1.07	-2.37
E	(+) _D - <u>trans</u> -[Co(en)(sdmn)Cl ₂] ⁺	2 N-CH ₃ , 4 CH ₂	-0.18	-0.17
F	<u>trans</u> -[Co(en)(R-sdmpn)Cl ₂] ⁺	2 N-CH ₃ , 4 CH ₂ ^b	-0.18	-0.13
G	<u>trans</u> -[Co(R-pn)(R-sdmpn)Cl ₂] ⁺ s-isomer	2 N-CH ₃ , 4 CH ₂ ^b	-0.18	-0.09
H	f-isomer		-0.18	-0.10
I	(+) _D - <u>trans,trans</u> -[Co(men)Cl ₂] ⁺	2 N-CH ₃ , 4 CH ₂	-0.18	-0.22
J	<u>trans,trans</u> -[Co(R-Nlmpn) ₂ Cl ₂] ⁺	2 N-CH ₃ , 4 CH ₂ ^b	-0.18	-0.20
K	<u>trans,trans</u> -[Co(R-N2mpn) ₂ Cl ₂] ⁺	2 N-CH ₃ , 4 CH ₂ ^b	-0.18	-0.05

^aThese values were used to calculate contributions used. ^bAssuming that the contribution for CHCH₃ is the same as for CH₂.

Using the values of 0.71 and -0.44, the expected values of the $A_{1g} \rightarrow E_g$ CD band for other complexes can be calculated. These are shown in Table VIII. As can be seen, agreement is not as good as found for the $A_{1g} \rightarrow A_{2g}$ bands. The largest disagreement occurs in cases where high energy $A_{1g} \rightarrow E_g$ components are significant compared to the low energy components used (i.e., for trans,trans- $[\text{Co}(\text{R-N}_2\text{mpn})\text{Cl}_2]^+$ (0.09 to -0.05) and for trans- $[\text{Co}(\text{R-sdmen})\text{Cl}_2]^+$ (0.53, 0.57 compared to -2.37, -2.42)).

3. The dinitro complexes and the validity of the hexadecadal rule

For the dinitro complexes all of the CD components in the $A_{1g} \rightarrow T_{1g}(O_h)$ region, which were separated into two or three bands in the dichloro complexes, overlap to give only one major band. Therefore, treatment of their activity using the hexadecadal rule would be expected to be very unreliable. In addition, Mason¹⁸ has pointed out that the rule will not hold if cylindrical symmetry about the metal-acid group bond direction does not exist. The Co-Cl moiety is cylindrically symmetric about the cobalt-chlorine bond while the Co-NO₂ moiety is not. Thus, the sign of the octants for the dinitro complexes cannot be assigned without knowing the positions of the nitro oxygens, and these may vary with different complexes.

With this in mind, the major $A_{1g} \rightarrow T_{1g}(O_h)$ CD band of the dinitro derivative can be examined (see Table IX). Since there is no reliable CD spectrum of trans- $\text{Co}(\text{pn})_2(\text{NO}_2)_2^+$ available^{8,10} it will not be considered. Proceeding, complexes with two cis N-CH₃ groups (C-E, Table IX) and complexes with two trans N-CH₃ groups (F-H)

TABLE IX

The CD Band Intensities for the Major $A_{1g} \rightarrow T_{1g}(O_h)$ Band
Near 22,000 cm^{-1} for the Dinitro Complexes

Complex Ion	Expected Contribution	Observed Band Intensity
A $(-)_D$ - <u>trans</u> - $[\text{Co}(\text{sdimen})_2(\text{NO}_2)_2]^+$	4 N-CH ₃ , 4 CH ₂	-1.62
B <u>trans</u> - $[\text{Co}(\text{R-sdimpn})_2(\text{NO}_2)_2]^+$ s-isomer	4 N-CH ₃ , 4 CH ₂ ^a	-2.75
C $(-)_D$ - <u>trans</u> - $[\text{Co}(\text{en})(\text{sdimen})(\text{NO}_2)_2]^+$	2 N-CH ₃ , 4 CH ₂	-1.23
D <u>trans</u> - $[\text{Co}(\text{en})(\text{R-sdimpn})(\text{NO}_2)_2]^+$	2 N-CH ₃ , 4 CH ₂ ^a	-1.23
E <u>trans</u> - $[\text{Co}(\text{R-pn})(\text{R-sdimpn})(\text{NO}_2)_2]^+$ f-isomer	2 N-CH ₃ , 4 CH ₂ ^a	-1.32
F $(-)_D$ - <u>trans,trans</u> - $[\text{Co}(\text{men})_2(\text{NO}_2)_2]^+$	2 N-CH ₃ , 4 CH ₂	-0.7
G <u>trans,trans</u> - $[\text{Co}(\text{R-Nlmpn})_2(\text{NO}_2)_2]^+$	2 N-CH ₃ , 4 CH ₂ ^a	-0.80
H <u>trans,trans</u> - $[\text{Co}(\text{R-N2mpn})_2(\text{NO}_2)_2]^+$	2 N-CH ₃ , 4 CH ₂ ^a	-0.92

^a Assuming that the contribution for CHCH₃ is the same as for CH₂.

should have similar activities for the same reasons as the dichloro complexes. Yet, the activity for these two groups of complexes are entirely different (e.g., the former group has band intensities near -1.3 and the later group near -0.8). The activity of complexes C-E are similar and the activity of F-H are similar. Each fact would suggest the C-CH₃ effect is small. Yet complexes A and B, which differ by two C-CH₃ groups have contrasting activity (-1.6 vs -2.75). Thus, it appears that a hexadecadal rule for the dinitro complexes does not exist which can be explained for the reasons given above.

4. Final observations of the CD results and suggestions of a need for further work

The hexadecadal rule can only be used to predict the sign and general magnitude of the activity of the dinitro complexes. This results for two possible reasons: (1) the component CD bands overlap to such a degree that the maximum of the resulting CD curve in this region does not realistically reflect the band intensity of any of the components; (2) the dinitro groups are not cylindrically symmetric about the cobalt-nitro bond, and because of this, the position of the nitro oxygen atoms, which will affect the activity, cannot be known with certainty. The hexadecadal rule must also be used with caution to predict the activity of the dichloro complexes in the $A_{1g} \rightarrow E_g(D_{4h})$ region for reason (1) above.

However, from all examples available to date, the $A_{1g} \rightarrow A_{2g}$ dichloro CD bands for bis(diamine) complexes are interpreted consistently using the principles of the hexadecadal rule. The small

deviations that do occur in CD intensities are most easily and consistently rationalized as arising because of small conformational variations. It can thus be safely stated that this regional sign rule predicts the induced activity of metal d-d transition for the dichloro complexes. In fact, there is reasonable agreement of the N-CH₃ contribution obtained here with that obtained from CD data for trans-dichloro complexes of N-methyl substituted triethylenetetramines.³⁶

It appears that more examples of the general trans-dichloro-tetramine type are needed in which more and different structural features can be related to activity for cobalt(III) complexes. Also, metals other than cobalt(III) should be studied. There is a need for more complexes of approximate D_{4h} symmetry to be studied for a possible applicable hexadecadal rule in which chelate rings do not lie in a tetragonal plane. Finally, it appears that the activity of many types of metal complexes (in which the activity has been explained in the past assuming chiral arrangement of chelate ring about the metal) should be re-examined in terms of several possible regional rules. It appears that regional sign rules may apply in all complexes where the metal d orbitals are not important in metal-ligand bonding (i.e., the d-d transitions are essentially metal transitions rather than metal-ligand transitions).

H. Secondary Nitrogen Inversion Rates

1. General considerations

Sargeson and coworkers have shown that optically active complexes

of N-methylethylenediamine²⁻⁵ and sarcosinate¹ undergo racemization and hydrogen isotope exchange at the secondary amine and that each process has the rate equation shown by equation 10.

$$\text{rate} = k [\text{complex}] [\text{OH}^-] \text{ where } k = k_{\text{rac}} \text{ or } k_{\text{deut}} \quad (10)$$

For the complex, (+)_D-trans,trans-[Co(men)₂(NO₂)₂]⁺, as an example, the mechanism is depicted in Figure 28. The first step of

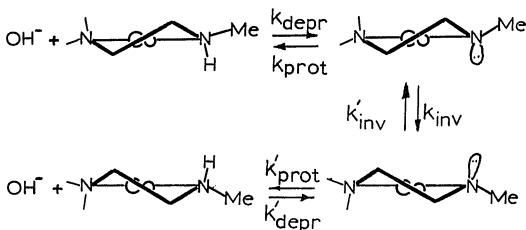


Figure 28. Proposed mechanism for racemization and deuteration of active trans,trans-[Co(men)₂(NO₂)₂]⁺. Only one men ring is shown. Structure (I) represents the dissymmetric form (dl or one enantiomer), and Structure (IV) represents the meso form.

hydrogen exchange is deprotonation by hydroxide ion, and this is followed by reprotonation (with hydrogen or deuterium). The reprotonation process is much faster than deprotonation, and consequently, the rate of formation of deuterated product in D₂O solution is equal to the rate of deprotonation. As depicted in Figure 28,

$$\text{rate of deprotonation} = k_{\text{depr}} [\text{I}] [\text{OH}^-] = \text{rate of deuteration.} \quad (11)$$

From a comparison of equation 10 with equation 11, it can be seen that k_{deut} , the rate constant for the overall deuterium exchange process is equal to k_{depr} , the rate constant of deprotonation.

In the racemization process, the active form, (I), is deprotonated, inverted at the asymmetric nitrogen center, and reprotionated, producing the meso form, (IV). The meso form then returns through this process, yielding (I), now the dl form. Deuteration and isomerization (meso \rightarrow dl) have both been shown to be rapid process compared to racemization. Thus, racemization can be treated as a rapid equilibrium (i.e., (I) \rightleftharpoons (II)) followed by the rate of determining nitrogen inversion step (i.e., (II) \rightarrow (III)). In equations 12-14, the rate of racemization is derived for the process in Figure 20.

$$\text{rate of racemization} = k_{\text{inv}} [(II)] \quad (12)$$

$$[(II)] = k_{\text{depr}}(k_{\text{prot}})^{-1} [(I)] [\text{OH}^-] \quad (13)$$

$$\text{rate of racemization} = k_{\text{inv}} k_{\text{depr}}(k_{\text{prot}})^{-1} [(I)] [\text{OH}^-] \quad (14)$$

From a comparison of equation 14 with equation 10, it is seen that the rate constant of racemization is that shown in equation 15. It

$$k_{\text{rac}} = k_{\text{inv}} k_{\text{depr}}(k_{\text{prot}})^{-1} \quad (15)$$

follows that the retention ratio, defined as the ratio of the rate constants of deuteration and racemization, is as indicated by equation 16.

$$\text{retention ratio} = k_{\text{deut}}(k_{\text{rac}})^{-1} = k_{\text{prot}}(k_{\text{inv}})^{-1} \quad (16)$$

The rate constants of protonation for a wide variety of oxygen and nitrogen lone pairs have been shown to be very similar (10^{10} - 10^{11} M⁻¹ sec⁻¹).⁴⁴ Thus, for a series of N-methyl substituted amine complexes, it seems reasonable to expect that values of k_{prot} for the secondary nitrogens would be very nearly equal.³ Consequently, if the mode of racemization and deuteration for these complexes is the same, then differences in their retention ratios should reflect changes in k_{inv} in a manner shown by equation 17.

$$\text{retention ratio} = k_{\text{deut}}(k_{\text{rac}})^{-1} \propto (k_{\text{inv}})^{-1} \quad (17)$$

With this in mind, the rates of deuteration and rate of loss of optical activity were examined for $(-)_D\text{-trans-}[\text{Co}(\text{sdmen})_2(\text{NO}_2)_2]^+$ and $(-)_D\text{-trans-}[\text{Co}(\text{en})(\text{sdmen})(\text{NO}_2)_2]^+$ in an attempt to correlate changes in the retention ratio with variations in the stereochemistry of the different chelated diamines.

Preliminary measurements on solutions of the bis(diamine) complex showed the loss of optical activity to be a complex process not clearly interpretable. In the pH range required for racemization, decomposition of the complex by base hydrolysis appeared to be the predominant reaction, and thus, measurements with this complex were not pursued further.

For the mixed(diamine) complex, racemization predominated although hydrolysis did occur at a competitive rate. Consequently, rates of racemization could be obtained from rates of loss of optical activity by making adjustments for hydrolysis effects, and the retention ratio for this complex was examined.

2. Hydrogen isotope exchange

Rate constants were obtained by following the growth of the methyl singlet from a doublet as the secondary amine is deuterated. Plots of $\log [(\text{peak height})_0 - (\text{peak height})_t]$ vs time gave reasonably linear curves (see Figure 21) from which the slope could be used to calculate the rate constants. The pseudo first-order rate constants, determined at three values of pH, varied with concentration of base in a reasonably linear manner as shown in Table X. The curves shown in Figures 29, 30, and 32 are those obtained from least-squares treatment of the data, as are the pseudo first-order rate constants listed in Tables X-XII. As expected, the kinetics of secondary amine deuteration of trans-[Co(en)(sdmen)(NO₂)₂]⁺ tended to approximate the rate law expected (equation 10).

Preliminary data taken for trans-[Co(sdmen)₂(NO₂)₂]⁺ showed similar behavior with somewhat faster rates than the mixed(diamine) complex.

TABLE X

Rate Constants of Deuterium Exchange^a for
trans-[Co(en)(sdmen)(NO₂)₂]⁺

pD ^b	k _{obsd} ^c (sec ⁻¹)	k _{deut} ^c (M ⁻¹ sec ⁻¹)
4.86	0.59 X 10 ⁻⁵	2.2 X 10 ⁴
5.22	1.77 X 10 ⁻⁵	2.8 X 10 ⁴
5.67	4.58 X 10 ⁻⁵	2.6 X 10 ⁴

^aTemp, 34.3°, 1 M KCl, acetate buffer. ^bpD = pH + 0.4. ^ck_{deut} =
k_{obsd} [D⁺] (K_{D₂O})⁻¹, K_{D₂O} = 3.8 X 10⁻¹⁵ at 34.3°.

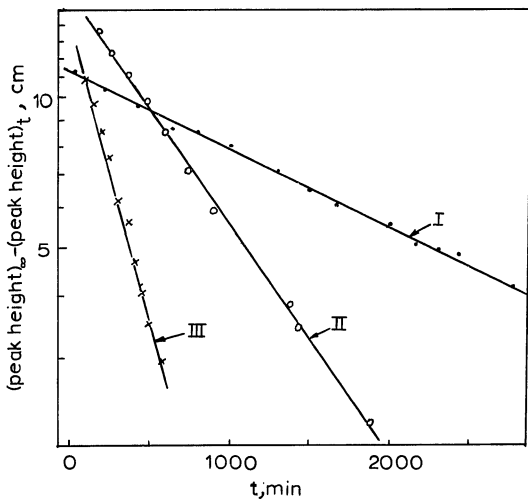
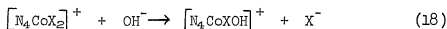


Figure 29. Plots of the logarithm of the peak height of the pmr N-methyl singlet vs time for $(-)\text{-trans-Co(en)(sdmen)(NO}_2)_2^+$ at a temp of 34.3° and 1M KCl. The pD is (I) 4.86; (II) 5.22; (III) 5.67.

3. Hydrolysis

It is well known⁴⁵ that trans-diacidotetraminecobalt(III) complex ions undergo hydrolysis in basic water solution as represented in equation 18. The rate equations observed are of the form of



equation 10 with $k = k_{hy}$.

This reaction for $(-)_D$ -trans- $[Co(en)(sdmen)(NO_2)_2]^+$ was studied in the pH region, 9.6-10. The expected pseudo first-order behavior was observed with the rate constants being determined from the slope of plots of $\log (A_t - A_\infty)$ vs time (see Figure 30). Values of A_∞ were recorded after 5 to 8 half-lives. There was a slight change in the value even after 8 half-lives. Presumably, this was a result of slow hydrolysis of the remaining nitro group. However, after 8 half-lives, the low energy d-d absorption peak at 446 nm had shifted to 492 nm, which is reasonable for hydrolysis of only one nitro group.^a The rate constants obtained in the pH range studied gave the expected dependence on $[OH^-]$ (see Table XI). It is surprising, however, that hydrolysis occurs at a noticeable rate in this region of pH. In contrast, Sargeson⁶ found that $(-)_D$ -trans,trans- $[Co(men)_2(NO_2)_2]^+$ undergoes hydrolysis at an insignificant rate in this pH range.

^a For trans- $[Co(en)_2(NO_2)_2]^+$, the low energy peak at 429 nm shifts to 549 nm in the diaquo complex.⁴⁶

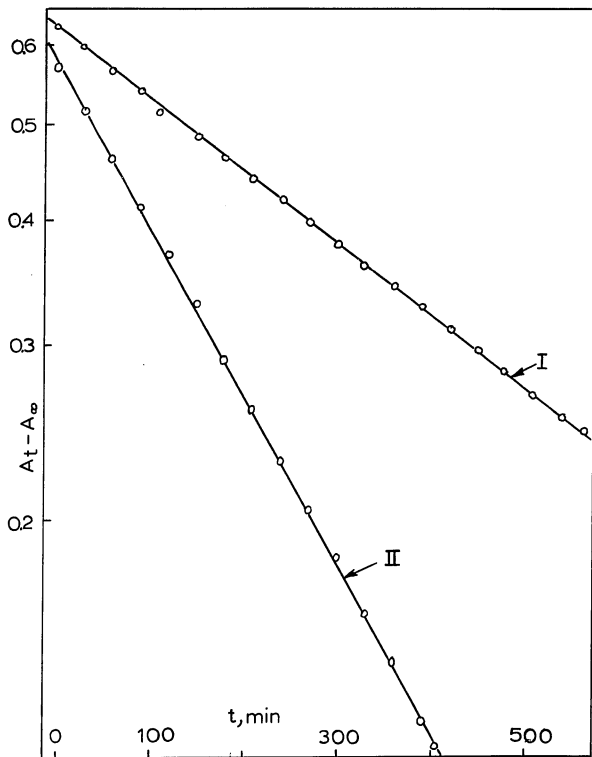


Figure 30. Plot of the logarithm of absorbance vs time for (-)-trans- $[\text{Co}(\text{en})(\text{sdmen})(\text{NO}_2)_2]^+$ at temp 34.3° , 0.5M KCl . The pH is (I) 9.60 ; (II) 9.94 .

TABLE XI

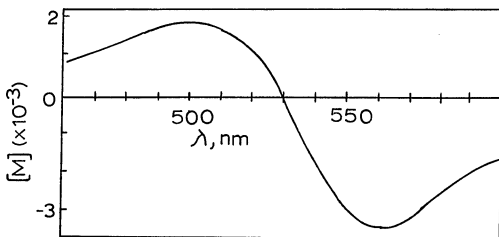
Rate Constants of Hydrolysis for $(-)_D\text{-trans-}[\text{Co(en)(sdmen)(NO}_2)_2]^+$ ^a

pH	k_{obsd}^d (sec^{-1})	k_{hy}^d ($\text{M}^{-1} \text{sec}^{-1}$)
9.94 ^b	$6.31, 6.28 \times 10^{-5}$	0.37
9.60 ^b	2.82×10^{-5}	0.36
9.74 ^c	2.74×10^{-5}	0.26

^aTemp, 34.3°. ^bKCl concentration, 0.5 M. ^cKCl concentration, 1M.
 $k_{\text{hy}} = k_{\text{obsd}}[\text{H}^+]$ (K_w)⁻¹, $K_w = 1.95 \times 10^{-14}$ at 34.3°.

4. Loss of optical activity and racemization

The rate of loss of optical activity (optical rotation) for $(-)_D\text{-trans-}[\text{Co(en)(sdmen)(NO}_2)_2]^+$ was measured polarimetrically over a range in pH of 9.26 to 10.10 at fifteen selected wavelengths in the region of 390-540 nm. The ORD curve is shown in Figure 31.

Figure 31. The ORD curve for $(-)_D\text{-trans-}[\text{Co(en)(sdmen)(NO}_2)]^+$.

Over this wavelength range, rate behavior varied markedly, and log

α vs time plots at most wavelengths did not show the linear behavior expected of racemization. This suggested that hydrolysis, which has been shown to be an important reaction in the pH range studied, must lead to an optically active hydrolysis product with a ORD curve different from that of the starting complex. This product can then racemize at its own rate. In the region of 500-510 nm, which is near the internal low energy maxima in the ORD curve (see Figure 30), good pseudo first-order behavior was observed for several half-lives in the entire range of pH covered in the study (see Figure 32). Presumably, this was because the optical activity of the hydrolysis product is close to zero in this wavelength region.

It is expected that a given pH, the levo dinitro complex would undergo the two pseudo first-order processes of hydrolysis and racemization. The rate equation would be equation 19.⁴⁷ The integrated form is shown by equation 20.

$$d[I] / dt = (k_{hy} + k_{rac}) [I] \quad (19)$$

$$\ln \left\{ \frac{[I]_0}{[I]_t} \right\} = (k_{hy} + k_{rac})t \quad (20)$$

The symbol (I) represents the starting levo dinitro complex. At wavelengths in which the activity of the hydrolysis product is small relative to that of the starting levo complex, the measured rotation would reflect the concentration of the l-complex alone, and equation 20 could be rewritten in the form of equation 21. These

$$\ln(\alpha_0/\alpha_t) = (k_{hy} + k_{rac})t \quad (21)$$

conditions would then yield linear curves for $\log \alpha$ vs time.

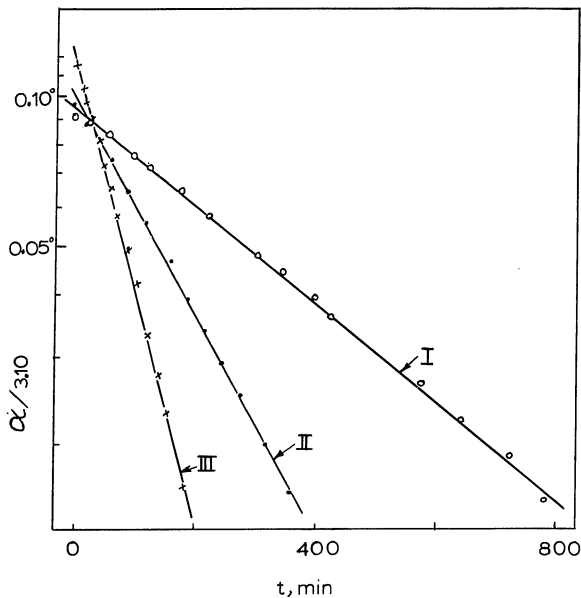


Figure 32. Plots of $\log \alpha$ vs time for $(-)\text{-trans-}[\text{Co(en)(sdmen)(NO}_2)_2]^+$ taken at 505 nm with a temp of 34.3° and $1M$ KCl. The pH is (I) 9.35; (II) 9.73; (III) 10.10.

It was impractical to prepare the optically active hydrolysis product to determine at which wavelengths it gave negligible rotations. However, linear plots were found for $\log \alpha$ vs time in the 500-510 nm region at all pH conditions studied, and it is assumed that this represented loss of activity of the levo complex and not the hydrolysis product. The rate constants determined (see Table XII) were approximately consistent with first-order base concentration behavior, consistent with equation 22 as the rate equation. More significant deviations were observed at a pH value of 10.10,

$$\text{rate} = (k_{\text{hy}} + k_{\text{rac}}) [(I)] [\text{OH}^-] \quad (22)$$

but these do not appear unreasonable. Such deviations were observed in the first-order base concentration relationship by Sargeson *et al.*³ for the racemization of $(-)_D\text{-trans,trans-[Co(men)}_2(\text{NO}_2)_2]^+$ at values of pH of 10.3 and greater. These were attributed to ion-association effects of the hydroxide ion. Measurements were performed at two concentration were of the most interest. These rate constants are reported at two wavelengths (505 nm and 510 nm) because the rate data at each wavelength gave the desired pseudo first-order behavior at each value of pH. Since a priori there is no reason to expect the rate constants obtained at one wavelength to be more accurate than those at the other wavelength, an average value was assumed to be the most accurate.

Therefore, $k_{\text{hy}} + k_{\text{rac}} = 0.78 \text{ M}^{-1} \text{ sec}^{-1}$ at 1 M KCl
 From Table XII, $k_{\text{hy}} = 0.26 \text{ M}^{-1} \text{ sec}^{-1}$ at 1 M KCl
 and, then, $k_{\text{rac}} = 0.52 \text{ M}^{-1} \text{ sec}^{-1}$ at 1 M KCl

TABLE XII

Rate Constants ^a of Loss of Optical Activity for (-)- <u>trans</u> - [Co(en)(sdmen)(NO ₂) ₂] ^{+b}				
KCl (M)	λ (nm)	pH	k_{obsd}^c (sec ⁻¹)	$(k_{\text{hy}} + k_{\text{rac}})^d$ (M ⁻¹ sec ⁻¹)
1.0	510	10.10	15.0, 15.9	0.63
		9.74	7.22, 8.14	0.72
		9.35	3.17, 3.27	0.74
	505	10.10	17.6, 19.5	0.75
		9.74	8.41, 9.56	0.84
		9.35	3.62, 3.75	0.84
0.5	510	9.60	8.49	1.09
		9.26	3.66	1.03
	500	9.94	23.9	1.41
		9.60	11.1, 12.2	1.50
		9.26	4.95	1.40

^a $k_{\text{hy}} + k_{\text{rac}}$. ^bTemp, 34.3°. ^c $k_{\text{obsd}} \times 10^5$. ^d $(k_{\text{hy}} + k_{\text{rac}}) = k_{\text{obsd}} [\text{H}^+] (k_w)^{-1}$, $k_w = 1.95 \times 10^{-14}$ at 34.3°.

5. Nitrogen inversion rates

From the treatment in the previous sections (1-4), it can be surmized that racemization and hydrogen exchange behavior at the secondary amine obey the same rate equation (equation 23) as expected

$$\text{rate} = k [(I)] [\text{OH}^-] \quad (23)$$

from previous studies of methyl amine complexes.¹⁻⁵ These processes, then, presumably have the same mechanism as proposed for (-)_D-trans, trans-[Co(men)₂(NO₂)₂]⁺ (Figure 20). For each, racemization involves inversion of one secondary nitrogen atom yielding the less stable meso form as an intermediate. This, then, will isomerize (at a faster rate) to the dl form.

From the results presented in sections 2-4, it is easily deduced that for (-)_D-trans-[Co(en)(sdmen)(NO₂)₂]⁺,

$$\text{retention ratio} = 48,000 \text{ at } 34.3^\circ, 1 \text{ M KCl}$$

For (+)_D-trans,trans-[Co(men)₂(NO₂)₂]⁺ the corresponding value is 89,000.³ From the treatment in section 1 (see equation 17) it is concluded that nitrogen inversion in the mixed complex of sdmen occurs at a faster than in the bis(men) complex.

In the introduction, it was mentioned that it is not certain at what point conformation interchange ($\delta \rightarrow \lambda$ or vice versa) of the diamine ring occurs. In Figure 28, for complexes of men it is shown that the conformation changes chirality as part of the inversion process ((II) \rightarrow (III), Figure 28). This allows the methyl groups

to be in the more stable equatorial position in both reactant and product. However, it is possible that this interchange occurs after nitrogen inversion as illustrated by Figure 33 for coordinate men.

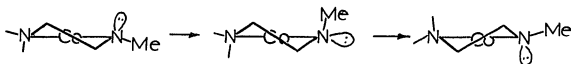


Figure 33. Nitrogen inversion followed by conformational interchange for coordinated deprotonated men.

For complexes of sdmen, it is not possible for conformational interchange to stabilize the inverted product in this way (see Figure 34).

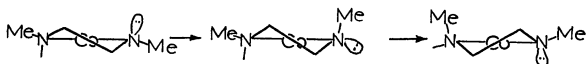


Figure 34. Nitrogen inversion followed by conformation interchange for coordinated deprotonated sdmen.

In either conformation, one of the N-methyl groups of sdmen must take a less stable axial position.

If conformational interchange occurs as part of the inversion process, one would expect $(+)\text{-}_D\text{-trans,trans-}[\text{Co}(\text{men})_2(\text{NO}_2)_2]^+$ to invert faster than $(-)\text{-}_D\text{-trans-}[\text{Co}(\text{en})(\text{sdmen})(\text{NO}_2)_2]^+$, reflecting the relatively more stable transition state of the former as a result of conformational interchange.

A comparison of the retention ratios of these complexes indicates this is not the case. The mixed complex, if anything, inverts somewhat faster. It is concluded that conformational interchange must occur after N-inversion, perhaps as pictured in Figures 33 and 34 for coordinated men and sdmen.

VI. SUMMARY

The complex ions, trans-dinitrobis(N,N' -dimethylethylenediamine)cobalt(III) and trans-dinitroethylenediamine-(N,N' -dimethylethylenediamine)cobalt(III) (N,N' -dimethylethylenediamine = sdmen) were prepared from a reaction of the diamines with sodium nitrite and cobalt(II) with aeration. The later complex ion was isolated by cationic-exchange column chromatography.

The proton magnetic resonance (pmr) spectra of these complexes were consistent with only one form being present in detectable amounts. There are seven and three stereoisomers possible for the former and later complex ions discussed above, respectively. These arise from the possible configurations that the asymmetric coordinated secondary amine nitrogen centers can take. Each complex isolated was resolved as the salt of the resolving agent, α -bromocamphor- η -sulfonate. The only form identified for each complex was an enantiomeric pair. For the mixed-diamine complex there is only one possible, but there are two possible for the bis-sdmen complex. The pmr evidence (i.e., one N-methyl and N-H resonance and one $AA'BB'$ methylene splitting pattern calculated for the experimental spectrum) indicated that the enantiomeric pair isolated has all four asymmetric nitrogen centers of one antipode with the same configuration.

The analogous dichloro complexes were prepared by reacting the dinitro complexes with concentrated hydrochloric acid. The resulting complexes were assigned the same configurations as the dinitro complexes from which they were prepared.

Similar complexes were prepared from (R)-N,N'-dimethylpropylene-diamine (R-sdmpn), which was prepared in two steps from R-propylene-diamine (R-pn). The trans-dinitro complex ions, $[\text{Co}(\text{R-sdmpn})_2(\text{NO}_2)_2]^+$, $[\text{Co}(\text{R-pn})(\text{R-sdmpn})(\text{NO}_2)_2]^+$, $[\text{Co}(\text{S-pn})(\text{R-sdmpn})(\text{NO}_2)_2]^+$ and $[\text{Co}(\text{en})(\text{R-sdmpn})(\text{NO}_2)_2]^+$, were prepared in a manner analogous to the complexes of sdmen (S-pn = (S)-propylenediamine). They were isolated using cationic-exchange column chromatography. The first three ions above were isolated as two stereoisomers. These were found to be distinguishable by small differences in the pmr spectra (i.e., there are small differences in the N-methyl resonance chemical shift). The last ion was found as only one form. The number of isomers formed in each case is consistent with the stereoselective coordination of R-sdmpn with an S configuration about each nitrogen center. This allows both the N-methyl and C-methyl groups to lie in favored equatorial conformations. The stereoisomers found in the first three cases arise from cis and trans placement of the C-methyl groups. However, on the basis of pmr evidence the stereoisomers could not at present be assigned the cis or trans C-methyl geometry with certainty. In addition to the dinitro complexes, the dichloro complexes were prepared from the dinitro complexes (except for the complex of S-pn).

The intensity of the $A_1 \rightarrow A_2$ tetragonal component CD band arising from the octahedral $A_1 \rightarrow T_1$ transition for the dichloro complexes prepared here was shown to obey a hexadecadal regional sign rule as suggested by Mason. The intensity in this region is primarily a result of the N-methyl substituents. For the $A_1 \rightarrow E$ tetragonal component CD band of the dichloro complexes and for the large

$A_1 \longrightarrow T_1$ octahedral component CD band for the dinitro complexes, the behavior was only qualitatively that predicted by a hexadecadal rule. However, in these cases, this was not unreasonable because of complex overlap of CD bands which results in a CD intensity which unreliably reflects the intensity of the overlapping bands. The agreement discussed here extends to the analogous complexes of mono N-methyl substituted diamine complexes.

Finally, the rates of N-deuteration and racemization were determined for $(-)\text{-trans-}[\text{Co(en)(sdmen)(NO}_2)_2]^+$ in a manner analogous to that reported by Buckingham, Marzilli and Sargeson in 1967 for $(+)\text{-trans,trans-dinitro-bis(N-methylethylenediamine)cobalt(III)}$. A comparison of the ratio of these rate constants for the two complexes suggested that the N-methyl nitrogen of the sdmen complex inverts its configuration about twice as fast as the other complex at 34.3° . This conclusion suggests that the diamine ring in these complexes has little effect on the rate of inversion at the nitrogen center.

VII. REFERENCES

1. B. Halpern, A.M. Sargeson, and K.R. Turnbull, J. Amer. Chem. Soc., **88**, 463 (1966).
2. D.A. Buckingham, L.G. Marzilli, and A.M. Sargeson, ibid, **89**, 825 (1967).
3. D.A. Buckingham, L.G. Marzilli, and A.M. Sargeson, ibid, **89**, 3428 (1967).
4. D.A. Buckingham, L.G. Marzilli, and A.M. Sargeson, ibid, **91**, 5227 (1969).
5. D.A. Buckingham and A.M. Sargeson, ibid, **90**, 6028 (1968).
6. D.A. Buckingham, L.G. Marzilli, and A.M. Sargeson, Inorg. Chem., **7**, 915 (1968).
7. Inorg. Chem., **9**, 1 (1970).
8. R.S. Cahn, C.K. Ingold, and V. Prelog, Angew. Chem. Intern. Ed. Engl., **5**, 385 (1966).
9. M. Saburi, Y. Tsujito, and S. Yoshikawa, Inorg. Nucl. Chem. Letters, **5**, 203 (1969).
10. M. Saburi, Y. Tsujito, and S. Yoshikawa, Inorg. Chem., **9**, 1476 (1970).
11. G.A. Barclay, E. Goldschmied, N.C. Stephenson, and A.M. Sargeson, Chem. Commun., 540 (1966).
12. Y. Saito and H. Iwasaki, Bull. Chem. Soc. Jap., **35**, 113 (1962).
13. E.J. Corey and J.C. Bailar, J. Amer. Chem. Soc., **81**, 2620 (1954).
14. H. Iwasaki and Y. Saito, Bull. Chem. Soc. Jap., **39**, 92 (1966).
15. C.J. Hawkins, Absolute Configurations of Metal Complexes, A volume in the Interscience Monographs on Chemistry. John Wiley and Sons, Inc., New York, NY, 1970. pp. 33-112.
16. W.T. Robinsom, D.A. Buckingham, G. Chandler, L.G. Marzilli, and A.M. Sargeson, Chem. Commun., 539 (1969).
17. C.J. Hawkins, ibid, 777 (1969).
18. S.F. Mason, ibid, 856 (1969).

19. J.A. Shellman, J. Chem. Phys., 44, 55 (1966).
20. R.B. Martin, J.M. Tsangaris, and J.W. Chang, J. Amer. Chem. Soc., 90, 821 (1968).
21. H. Reihlen, E. Weinbrenner, and G.V. Hessling, Ann., 494, 143 (1932).
22. W. Theilacker, Z. Anorg. Allegan. Chem., 234, 161 (1937).
23. F.P. Dwyer and F.L. Shulman, J. Amer. Chem. Soc., 81, 290 (1959).
24. J.C. Bailar, H.B. Jonassen, and A.D. Gott, ibid, 74, 313 (1952).
25. W.E. Cooley, C.F. Liu, and J.C. Bailar, ibid, 81, 4199 (1959).
26. L.A. Kane-Maguire and T.E. MacDermott, Inorg. Chem., 7, 768 (1968).
27. This program is described in P.F. DeTar, Ed., "Computer Programs for Chemistry," Vol. I, W.A. Benjamin, Inc., New York, NY, 1968, pp. 10.
28. R. Lumry, E.L. Smith, and R.R. Glantz, J. Amer. Chem. Soc., 73, 4330 (1951).
29. P.K. Glascoe and F.A. Long, J. Phys. Chem., 64, 188 (1960).
30. S. Yano, H. Ito, Y. Koike, J. Fujita, and K. Saito, Bull. Chem. Soc. Jap., 42, 3184 (1969).
31. J.K. Beattie and H. elsbernd, J. Amer. Chem. Soc., 92, 1946 (1970).
32. M. Barfield, J. Chem. Phys., 41, 3825 (1964).
33. L.F. Druding, Coordin. Chem. Rev., 3, 409 (1968).
34. J.R. Gollogly and C.J. Hawkins, Inorg. Chem., 8, 1168 (1969).
35. J.R. Gollogly, C.J. Hawkins, and J.K. Beattie, ibid, 10, 318 (1971).
36. M. Gato, A. Okubo, T. Sawai, and S. Yoshikawa, ibid, 9, 1488 (1970).
37. J.C. Dabrowiak and D.W. Cooke, J. Amer. Chem. Soc., 92, 1097 (1970).
38. C.J. Hawkins, E. Larsen, and I. Olsen, Acta Chem. Scand., 19, 1915 (1965).
39. Reference 15, pp 148-227.
40. R.A.D. Wentworth and T.S. Piper, Inorg. Chem., 4, 202 (1965).
41. J.I. Legg and D.W. Cooke, Inorg. Chem., 6, 7004 (1967).

42. L.N. Schoenberg, D.W. Cooke, and C.F. Liu, Inorg. Chem., 7, 2386 (1968).
43. S.K. Hall and B.E. Douglas, Inorg. Chem., 7, 333 (1968).
44. E.F. Caldin, Fast Reactions in Solution, John Wiley and Sons, New York, NY, 1964, pp 263.
45. F. Basolo and R.G. Pearson, Mechanisms of Inorganic Reactions, Wiley and Sons, New York, NY, 1967, pp 177-193, 261-5.
46. R.A.D. Wentworth and T.S. Piper, Inorg. Chem., 4, 709 (1965).
47. A.A. Frost and R.G. Pearson, Kinetics and Mechanism, John Wiley and Sons, New York, NY, 1961, pp 161.