Stereochemistry and Circular Dichroism of Some Cobalt(III) Complexes with Ethylenediamine-N, N’-Diacetic Acid and N, N’-Dimethylethylenediamine-N,N’-Diacetic Acid

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Godfrey C. Mbah
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To

my mother, Amazu,

who made it all possible
TABLE OF CONTENTS

ACKNOWLEDGEMENTS iii
LIST OF TABLES viii
LIST OF FIGURES ix
LIST OF ABBREVIATIONS xi

INTRODUCTION 1

STATEMENT OF PROBLEM 9

STEREOCHEMISTRY OF THE LIGANDS AND THEIR CHELATE RINGS 10

EXPERIMENTAL 13

A. Materials 13

B. Preparation of the Ligands 14

1. R-1,2-propanediamine 14

2. R-Diethyl-1,2-propanediaminebis(carbamate) 14

3. R-N,N'-dimethyl-1,2-propanediamine 15

4. N-N'-dimethylethlenediamine-N,N'-diacetic acid 15

C. Preparation of the Complexes 17

1. trans-Ethlenediamine-N,N'-diacetato (N-methylethlenediamine)cobalt(III) nitrate, trans-[Co(Meen)EDDA]NO₃ 17

2. Resolution of trans-[Co(Meen)EDDA]⁺ 18

3. Conversion of (-)-D-trans-[Co(Meen)EDDA]H₂O to trans-[Co(Meen)EDDA]ClO₄⁻•0.5H₂O 19

4. Conversion (+)-D-trans-[Co(Meen)EDDA]H₂O to (+)-D-trans-[Co(Meen)EDDA]ClO₄⁻•0.5H₂O 19
TABLE OF CONTENTS (continued)

5. **trans-Ethylendiamine-N,N'-diacatato(N,N'-
dimethyl ethylendiamine)cobalt(III) nitrate,**
   trans-[Co(sdmeen)EDDA]NO₃  19

6. Resolution of **trans-[Co(sdmeen)EDDA]NO₃**  20

7. Conversion of **(-)ₜrans-[Co(sdmeen)EDDA]**
   H₂O to **(-)ₜrans-[Co(sdmeen)EDDA]NO₃**  21

8. Conversion of **(+)-trans-[Co(sdmeen)EDDA]**
   H₂O to **(+)-trans-[Co(sdmeen)EDDA]NO₃**  21

9. **trans-Ethylendiamine-N,N'-diacatato(2-
methyl-1,2-diaminopropane)cobalt(III) nitrate monohydrate, trans-[Co(2-Mepn)EDDA]**
   NO₃·H₂O  19

10. Resolution of **trans-[Co(2-Mepn)EDDA]NO₃·H₂O**  22

11. Conversion of **(-)-trans-[Co(2-Mepn)EDDA]**
    H₂O to **(-)-trans-[Co(2-Mepn)EDDA]NO₃**  22

12. Conversion of **(+)-trans-[Co(2-Mepn)EDDA]**
    H₂O to **(+)-trans-[Co(2-Mepn)EDDA]NO₃**  22

13. **(-)-trans-Ethylendiamine-N,N'-diacatato**
    (R-N,N'-dimethyl-1,2-propanediamine) cobalt(III) perchlorate, **(-)ₜrans-[Co(R sdmeen)EDDA]ClO₄**  23

14. **(+)-trans-Ethylendiamine-N,N'-diacatato(R-N, N'-dimethyl-1,2-pepanediamine) cobalt(III)**
    monohydrogen perchlorate **(+)-trans-[Co(R -sdmeen)EDDA]ClO₄·HClO₄**  24

15. **trans-Ethylendiamine-N,N-diacatato(N,N-diethyl-
    ethylendiamine)cobalt(III) nitrate, trans-**
    [Co(udmeen)EDDA]NO₃  24

16. Resolution of **trans-[Co(udmeen)EDDA NO₃·5H₂O**  25

17. **trans-N,N'-Dimethyleneethylendiamine-N,N'-diacatato-
    (N-methyl ethylendiamine)cobalt(III), nitrate dihydrate trans-[Co(Meen)DMEDDA]NO₃·2H₂O**  25
**TABLE OF CONTENTS (Continued)**

18. Resolution of \( \text{trans-}[\text{Co(Meen)}\text{DMEDDA}]\text{NO}_3\cdot2\text{H}_2\text{O} \)  
19. Conversion of \( (+)_D\text{trans-}[\text{Co(Meen)}\text{DMEDDA}]\text{H}_{\text{art}} \) to \( (+)_D\text{trans-}[\text{Co(Meen)}\text{DMEDDA}]\text{ClO}_4 \)
20. Conversion of \( (-)_D\text{trans-}[\text{Co(Meen)}\text{DMEDDA}]\text{H}_{\text{art}} \) to \( (-)_D\text{trans-}[\text{Co(Meen)}\text{DMEDDA}]\text{ClO}_4 \)
21. \( \text{trans-}N,N'_-\text{Dimethylethlenediamine-}N,N'_-\text{diacetato}\) (2-methyl-1,2-propanediamine)cobalt (III) nitrate dihydrate, \( \text{trans-}[\text{Co(2-Mepn)}\text{DMEDDA}]\text{NO}_3\cdot2\text{H}_2\text{O} \)
22. Resolution of \( \text{trans-}[\text{Co(2-Mepn)}\text{DMEDDA}]\text{NO}_3 \)
23. Conversion of \( (+)_D\text{trans-}[\text{Co(2-Mepn)}\text{DMEDDA}]\text{H}_{\text{art}} \) to \( (+)_D\text{trans-}[\text{Co(2-Mepn)}\text{DMEDDA}]\text{ClO}_4 \)
24. Conversion of \( (-)_D\text{trans-}[\text{Co(2-Mepn)}\text{DMEDDA}]\text{H}_{\text{art}} \) to \( (-)_D\text{trans-}[\text{Co(2-Mepn)}\text{DMEDDA}]\text{ClO}_4 \)
25. \( \text{trans-}N,N'_-\text{Dimethylethlenediamine-}N,N'_-\text{diacetato}\) (\(N,N'_-\text{dimethylethlenediamine}\))cobalt(III) nitrate monohydrate \( \text{trans-}[\text{Co(sdmeen)}\text{DMEDDA}]\text{NO}_3\cdot\text{H}_2\text{O} \)
26. \( (+)_D\text{trans-}N,N'_-\text{Dimethylethlenediamine-}N,N'_-\text{diacetato-(}R-1,2\text{-propanediamine)cobalt(III)}\) perchlorate, \( \text{trans-}[\text{Co((R)-pn)}\text{DMEDDA}]\text{ClO}_4 \)
27. \( (+)_D\text{trans-}N,N'_-\text{Dimethylethlenediamine}\) \(N,N'_-\text{diacetato-(}R-N,N'_-\text{dimethyl-1,2-propane-}
\text{diamine)cobalt(III)perchlorate monohydrate \( \text{trans-}[\text{Co(R-sdmeen)}\text{DMEDDA}]\text{ClO}_4\cdot\text{H}_2\text{O} \)

D. Electronic Absorption Spectra  
E. Optical Rotations  
F. Circular Dichroism Spectra  
G. Proton Magnetic Resonance Spectra  

RESULTS AND DISCUSSION

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TABLE OF CONTENTS (Continued)

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Preparations</td>
<td>33</td>
</tr>
<tr>
<td>B. Spectra</td>
<td>38</td>
</tr>
<tr>
<td>1. Ultraviolet-visible Spectra</td>
<td>38</td>
</tr>
<tr>
<td>2. Circular Dichroism Spectra</td>
<td>38</td>
</tr>
<tr>
<td>3. Proton Magnetic Resonance Spectra</td>
<td>42</td>
</tr>
<tr>
<td>C. Stereochemistry and Chelate Ring Conformation</td>
<td>71</td>
</tr>
<tr>
<td>1. Stereochemical Consideration</td>
<td>71</td>
</tr>
<tr>
<td>2. Conformation of the Bidentate Chelate Ring</td>
<td>76</td>
</tr>
<tr>
<td>D. Assignment of the Absolute Configurations to the Complexes</td>
<td>82</td>
</tr>
<tr>
<td>1. Complexes with $\Delta(C_2)$ Absolute Configuration</td>
<td>84</td>
</tr>
<tr>
<td>2. Complexes with $\Lambda(C_2)$ Absolute Configuration</td>
<td>85</td>
</tr>
<tr>
<td>E. Circular Dichroism and the Hexadecadal Rule</td>
<td>91</td>
</tr>
<tr>
<td>1. EDDA Complexes and the Validity of the Hexadecadal Rule in the $A_{1g}$-$A_{2g}$ CD Region</td>
<td>95</td>
</tr>
<tr>
<td>2. EDDA Complexes and the Validity of the Hexadecadal Rule in the $A_{1g}$-$E_g$ CD Region</td>
<td>96</td>
</tr>
<tr>
<td>3. DMEDDA Complexes and the Validity of the Hexadecadal Rule in $A_{1g}$-$A_{2g}$ CD Region</td>
<td>96</td>
</tr>
<tr>
<td>4. DMEDDA Complexes and the Validity of the Hexadecadal Rule in $A_{1g}$-$E_g$ CD Region</td>
<td>97</td>
</tr>
<tr>
<td>SUMMARY</td>
<td>103</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>105</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>109</td>
</tr>
</tbody>
</table>
### LIST OF TABLES

<table>
<thead>
<tr>
<th>TABLE</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Stereoisomers of trans-[Co(diamine)EDDA]† Prepared and Identified</td>
<td>34</td>
</tr>
<tr>
<td>II</td>
<td>Stereoisomers of trans-[Co(diamine)DMEDDA] Prepared and Identified</td>
<td>35</td>
</tr>
<tr>
<td>III</td>
<td>The Electronic Absorption Spectra of the Complexes</td>
<td>40</td>
</tr>
<tr>
<td>IV</td>
<td>Circular Dichroism Data for EDDA Complexes</td>
<td>48</td>
</tr>
<tr>
<td>V</td>
<td>Circular Dichroism Data for DMEDDA Complexes</td>
<td>49</td>
</tr>
<tr>
<td>VI</td>
<td>Resonance Frequency Assignment and Integration Values from the NMR Spectra</td>
<td>67</td>
</tr>
<tr>
<td></td>
<td>of the Complexes</td>
<td></td>
</tr>
<tr>
<td>VII</td>
<td>Absolute Configuration of the $\Delta(C_2)$ Complexes</td>
<td>87</td>
</tr>
<tr>
<td>VIII</td>
<td>Absolute Configuration of the $\Lambda(C_2)$ Complexes</td>
<td>90</td>
</tr>
<tr>
<td>IX</td>
<td>Calculated CD Intensities for $A_{1g}-A_{2g}$ for $\Lambda(C_2)$ EDDA</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>Complexes</td>
<td></td>
</tr>
<tr>
<td>X</td>
<td>Calculated CD Intensities for $A_{1g}^{-}-E_{g}$ CD Band for $\Lambda(C_2)$</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>EDDA Complexes</td>
<td></td>
</tr>
<tr>
<td>XI</td>
<td>Calculated CD Intensities for $A_{1g}-A_{2g}$ CD Band for $\Delta(C_2)$</td>
<td>99</td>
</tr>
<tr>
<td></td>
<td>DMEDDA Complexes</td>
<td></td>
</tr>
<tr>
<td>XII</td>
<td>Calculated CD Intensities for $A_{1g}^{-}-E_{g}$ CD Band for $\Delta(C_2)$</td>
<td>101</td>
</tr>
<tr>
<td></td>
<td>DMEDDA Complexes</td>
<td></td>
</tr>
</tbody>
</table>
LIST OF FIGURES

FIGURE

1. Structures of the Enantiomers of [Co(NH3)4(Meen)]3+ 1
2. Structures of Stereoisomers of trans, trans-[Co(Meen)2(NO2)2]3+ 2
3. Two Possible Conformations that Result When (S)-N'-Mepn Coordinates to a Metal Ion. 5
4. Regional Sign Arrangement for Contribution to the Activity of the A1g-A2g(D4h) CD Bands for Dichlorotetraamine Cobalt(III) Ions 7
5. The Regional Sign Arrangement Above the Co-N4 Plane of Contributions by Diamine Moieties to the A1g-A2g(D4h) CD Band in trans, trans-[Co(Meen)2C22]+ 8
6. Absolute Configuration of (-)D-1,2-propanediamine and N,N'-dimethyl-1,2-propanediamine 10
7. Skew Conformations of Chelated Ethylenediamine 12
8. Possible Configuration of Coordinated EDDA and DMEDDA 36
10. CD Spectra for (+)D- and (-)D-trans-[Co(sdmeeen)EDDA]+ 43
11. CD Spectra for (-)D-trans-[Co(R-sdmepn)EDDA]+ 44
12. CD Spectra for (+)D- and (-)D-trans-[Co(Meen)DMEDDA]+ 45
13. CD Spectra for (+)D-trans-[Co(2-Mepn)DMEDDA]+ 46
14. CD Spectra for (+)D-trans-[Co(R-pn)DMEDDA]+ 47
15. The NMR Spectrum of trans-[Co(Meen)EDDA]+ 57
16. The NMR Spectrum of trans-[Co(udmeen)EDDA]+ 58
17. The NMR Spectrum of trans-[Co(sdmeeen)EDDA]+ 59
18. The NMR Spectrum of trans-[Co(R-sdmepn)EDDA]+ 60

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LIST OF FIGURES (Continued)

FIGURE

19  The NMR Spectrum of trans-[Co(R-sdmepn)DMEDDA]⁺ 61
20  The NMR Spectrum of trans-[Co(R-pn)DMEDDA]⁺ 62
21  The NMR Spectrum of trans-[Co(Meen)DMEDDA]⁺ 63
22  The NMR Spectrum of trans-[Co(sdmeen)DMEDDA]⁺ 64
23  The NMR Spectrum of trans-[Co(2-Mepn)EDDA]⁺ 65
24  The NMR Spectrum of trans-[Co(2-Mepn)DMEDDA]⁺ 66
25  Possible Conformation of N-C-C-N Chelate Ring 71
26  Possible Orientation of the Methyl Group in Co-ordinated R-pn 72
27  Absolute Configuration of trans-[Co(en)EDDA]⁺ 73
28  Diagram of A(C2) and A(C2) Complexes of trans-[Co(R-pn)EDDA]⁺ 74
29  Partial Racemization of A(C2) Complex 79
30  The Energy Level Splitting in O₃ and Tetragonal (trans) Complex in the d-d Transition Region 82
31  Diagram on A(C2) Complex 86
32  Diagram of an A(C2) Complex 89
33  Partial Regional Sign Arrangement Above the Co-N₄ Plane for the A₁g-A₂g(D₄h) CD Band 92
34  Regional Sign Arrangement Above the Co-N₄ Plane for A₁g-A₂g(D₄h) CD Band 93
LIST OF ABBREVIATIONS

CD Circular dichroism
en Ethylenediamine
Meen N-Methylethylenediamine
R-pn R-1,2-Propanediamine
2-Mepn 2-Methyl-1,2-propanediamine
sdmeen N,N'-Dimethylethylenediamine
udmeen N,N'-Dimethylethylenediamine
R-sdmeen R-N,N'-Dimethyl-1,2-propanediamine
EDTA Ethylenediaminetetraacitic acid
EDDA Ethylenediamine-N,N'-diacetic acid anion
DMEDDA N,N'-Dimethylethylenediamine-N,N'-diacetic acid anion
S-N,Mepn (S)-N1-Methyl-1,2-propanediamine
R-chxn R-1,2-trans-diaminocyclohexane
L-3,8-Me2-trien L-3,8-dimethyltriethylenetetraamine
Sar Sarcosinate anion
NMR nuclear magnetic resonance
UV ultraviolet
M$_c$ megacycles
INTRODUCTION

Within the last fifteen years a series of transition metal complexes containing secondary amines\textsuperscript{1-8} has been prepared. The complex ion, $[\text{Co(NH}_3\text{)}_4\text{Meen}]^{3+}$,\textsuperscript{2} has been shown to exist as a pair of enantiomers (shown in Figure 1) and has been resolved (Meen=N-methyl-ethylenediamine). Likewise, the $[\text{Co(NH}_3\text{)}_4\text{Sar}]^{2+}$ ion\textsuperscript{1} and $[\text{Pt(en)}^-\text{Meen}]^{2+}$ ion\textsuperscript{2} have also been resolved (Sar = Sarcosinate ion). In these complexes, the dissymmetry arises solely as a result of the coordinated asymmetric nitrogens. For the same reason, a meso form

![Figure 1](image_url)

Figure 1 Structures of the enantiomers of $[\text{Co(NH}_3\text{)}_4\text{(Meen)}]^{3+}$ and an enantrimeric pair of the trans, trans-$[\text{Co(Meen)}_2(\text{NO}_2)_2]^+$ ion\textsuperscript{3} were isolated and characterized as having the structure shown in Figure 2. The meso form has the two secondary amine nitrogens with mirror image configuration whereas the enantiomers have the two nitrogen atoms with the same configuration.
Figure 2. Structures of stereoisomers of \textit{trans-}[\text{Co(Meen)}_2(\text{NO}_2)_2]^+.
I and II are enantiomers; III is a meso form.
For some time the origin of optical activity in the d-d metal transition region for amine complexes possessing asymmetric nitrogen centers was a point of controversy. Buckingham, and coworkers assigned the absolute configuration of \((-)_D\)-trans, trans-[Co(Meen)\(_2\)Cl\(_2\)]\(^+\), which they prepared from the dextro dinitro complex. Their assignment was based on a comparison of the CD (circular dichroism) spectrum for this complex ion with those of the complexes \((+_D\)-trans-[Co(L-3,8-Me\(_2\)trien)Cl\(_2\)]\(^+\), \((+_D\)-trans-[Co(Trien)Cl\(_2\)]\(^+\), trans-[Co(R-pn)\(_2\)-Cl\(_2\)]\(^+\), and trans-[Co(R-chxn)\(_2\)Cl\(_2\)]\(^+\) (L-3,8-Me\(_2\)trien = L-3,8-dimethyltriethylene-tetraamine, R-pn = 1,2-propanediamine and R-chxn = R-trans-1,2-cyclohexanediame). From X-ray studies, the gauche (or skew) diamine side chain ring conformations in the first two complexes are known to be the same as Structure I in Figure 1 as are the diamine rings of the latter complexes. This conformation is called \(\delta\) conformation. The opposite conformation (Structure II in Figure 3) is called the \(\lambda\) conformation. Buckingham and coworkers 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 \((-)_D\)-trans, trans-[Co(Meen)\(_2\)Cl\(_2\)]\(^+\) as \(\lambda\) because the CD curve bears a mirror image relation to those of the other trans-diacido-tetraamine complexes which are known to have \(\delta\) ring conformations. From conformational consideration, it is known that the N-methyl group of N-methylethylene diamine prefers an equatorial conformation. Thus, the secondary nitrogen configurations in \((-)_D\)-trans, trans-[Co(Meen)\(_2\)Cl\(_2\)]\(^+\) were assigned \(S\) configurations (as in Structure II in Figure 1).
From a study of stereospecific coordination of N$_1$-Methyl-S-1,2-propanediamine (S-N$_1$-Mepn), Saburi and coworkers$^{14,15}$ concluded that Buckingham and coworkers has assigned the absolute configuration of (-)$_D$-trans,trans-[Co(Meen)$_2$(Cl$_2$)]$^+$ incorrectly. When N$_1$-methyl-S-1,2-propanediamine coordinates to a metal ion, there are two possible gauche ring conformations (X and 6) which the chelate ring can assume. However, X-ray$^{16,17}$ and conformational analysis$^{18-20}$ studies of complexes of S-1,2-propanediamine suggest that the C-methyl group always prefers to be in an equatorial position with respect to the metal chelate ring resulting in a 6 ring conformation.

The N-methyl nitrogen can assume one of two possible configurations as shown in Figure 3. Structure I has the N-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-ray$^{21}$ and conformational analysis studies$^{2,20}$ of complexes of N-methylethylenediamine suggest that N-methyl prefers equatorial orientation. Since this diamine has been shown by Saburi and coworkers$^{15}$ to coordinate stereospecifically, this preference must be pronounced. In order for N-methyl and C-methyl on the asymmetric carbon atom of known S absolute configuration both to be equatorial, the ring conformation must be 6 and the nitrogen configuration must be R for the trans, trans-[Co(S-N$_1$-Mepn)$_2$Cl$_2$]$^+$.

The CD curve for this complex is very similar to that for (-)$_D$-trans, trans-[Co(Meen)$_2$Cl$_2$]$^+$ in the 550nm region. This resulted in Saburi and coworkers assigning an R nitrogen configuration and a 6 ring conformation to the N-methylmethylenediamine complex$^{14}$. This assignment was in conflict with that made by Buckingham and coworkers$^9$. 

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Figure 3. Two possible conformations that result when S-N$_1$-Mepn coordinates to a metal ion. The conformations shown are those resulting from preferential placement of C-methyl equatorially.
A resolution of this conflict came shortly thereafter. The structure of $(-)_D^{\text{-trans}}$ trans-[Co(Meen)$_2$Cl$_2$]$ClO_4\cdot0.5H_2O$ in a single crystal was determined by the anomalous dispersion X-ray diffraction technique. The diamine rings were found to be in $\delta$ conformations and the nitrogen configurations were $R$ with the $N$-methyl group in an equatorial position. (Buckingham, and coworkers assignment from the comparison of the CD curve with those of other $\text{trans}$-dichlorotetraamine complexes which possessed no $N$-methyl substituent was therefore incorrect.)

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

Mason concurrently proposed a somewhat different explanation. He believed that the activity of $\text{trans}$-diacidotetraamine complexes should in general obey a regional sign rule. He suggested that the $A_{1g} - A_{1g}(D_{4h})$ CD band near 450nm for $(-)_D^{\text{-trans}}$ trans-[Co(Meen)$_2$Cl$_2$]$^+$, trans-[Co(R-pn)$_2$Cl$_2$]$^+$ and trans, trans-[Co(S-N-Mepn)$_2$Cl$_2$]$^+$ obey a hexadecadal rule. Applying this rule, the regions of space above and below the metal-amine plane are divided into two sets of
the asymmetric carbon atoms and (b) the asymmetric nitrogen atoms. In order to account for the effects discussed above, he concluded that the contributions from the secondary nitrogen atoms were much greater than the other two effects combined and were of opposite sign.

Mason\(^{23}\) concurrently proposed a somewhat different explanation. He believed that the activity of \textit{trans}-diacidotetraamine complexes should in general obey a regional sign rule. He suggested that the \(A_{1g} - A_{2g}(D_{4h})\) CD band near 450 nm for (-)\(_{D}^{\text{trans,trans}}\) [Co(Meen)\(_2\)Cl\(_2\)]\(^+\), \textit{trans}–[Co(R–pn)\(_2\)Cl\(_2\)]\(^+\) and \textit{trans}, \textit{trans}–[Co(S–N\(_1\)–Mepn)\(_2\)Cl\(_2\)]\(^+\) obey 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 4 for \(A_{1g} - D_{2g}(D_{4h})\) component band. For the above mentioned complex ions

\[
\begin{array}{c}
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\begin{array}{c}
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\]

\text{Figure 4. Regional sign arrangement for contribution to the activity of the } A_{1g} - A_{2g}(D_{4h}) \text{ CD band for dichlorotetraamine cobalt (III) ions. Diagrams I and II are for above and below the tetragonal plane respectively.}

which possess \(\delta\) chelate ring conformation and \(R\) absolute configuration for the asymmetric nitrogen atoms, the N-methyl substituent

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lies in negative regions while the ring carbon and C-methyl moieties lie in positive regions, Figure 5. In addition, it

![Diagram](image)

**Figure 5.** The regional sign arrangement above the Co-N$_4$ plane of contributions by diamine moieties to the $A_{1g}$-$A_{2g}$($D_{4h}$) $CD$ band in (-)D-trans, trans-[Co(Meen)$_2$Cl$_2$]$^+$. Carbon atoms above the plane (+Z) are represented as solid circles (●) and below (-Z) as open circles (○). The signs shown are for substituent contribution in the +Z space. Those in the -Z space are of opposite sign.

is easily seen from the molecule models that the N-methyl groups lie further above the CoN$_4$ plane than the methylene and methyl-methylene ring moieties and therefore should contribute more to the activity. A hexadecadal array of opposite sign to that shown in Figure 4 describes the $A_{1g}$-$E_g$($D_{4h}$) low energy component in the $A_{1g}$-$T_{1g}$($O_h$) transition region.

Mason's approach is more general than that proposed by Hawkins. Any dissymmetric trans-diacidotetraamine can be described assuming the magnitude of the contributing substituents is known.

The hexadecadal rule has a theoretical basis as Shellman$^{24}$ has shown. It appears that a hexadecadal rule should predict the activity of d-d bands of trans-diacidotetraamine complexes.

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STATEMENT OF PROBLEM

In the early seventies Cooke and Tiethof\textsuperscript{8} prepared a series of trans-diacidobis(diamine)cobalt(III) complexes of $N,N'$-dimethyl-ethylenediamine and $N,N'$-dimethyl-1,2-propanediamine for the purpose of evaluating the two theories\textsuperscript{22,23} on the origin of optical activity in dissymmetric tetragonal complexes. They found that the circular dichroism data for these complexes supported the two theories. In the case of the hexadecadal rule of Mason\textsuperscript{23}, numerical values for substituent contribution could be predicted in some cases using this rule. It is therefore of some interest to prepare different but similar complexes to further test these theories\textsuperscript{25}.

A series of cobalt complexes containing diamines and either ethylenediamine-$N,N'$-diacetic acid or $N,N'$-dimethyl-ethylenediamine-$N,N'$-diacetic acid were prepared for this purpose.

The complexes were prepared and resolved into enantiomers. The optical isomers were converted to nitrate or perchlorate salts. For the complexes of $R$-1,2-propanediamine and $R$-$N,N'$-dimethyl-1,2-propanediamine the solution from the initial preparation was optically active. This is due to the stereoselective coordination of the $N$-methyl nitrogen atom in the active diamine.

Before the circular dichroism data could be analyzed the stereochemistry of the complexes had to be ascertained. This was done by the use of proton magnetic resonance data. The nitrates salts generally were soluble enough in $D_2O$ to give good spectra. For the perchlorate salts it was necessary to convert them to chloride salts before good spectra could be obtained.
The secondary nitrogen atoms in the ligands such as N,N'-dimethyl-1,2-propanediamine are not asymmetric centers until they coordinate to the metal center. When they do, they theoretically introduce a large number of stereochemical possibilities. However not all of these are realized because of stereospecific coordination of the ligands or chelate ring constraints. For example EDDA or DMEDDA has two asymmetric nitrogen centers on coordination. These two nitrogen centers can be either R or S with theoretically three possible combinations; R,R, S,S, or R,S if the two nitrogens are chemically equivalent. (The R,S combination will result in a meso form if there are no other asymmetric centers). It has been found that the nitrogens adopt the same configuration both R,R or S,S, thus giving only a d,l pair if the two nitrogens are the only asymmetric centers. If there are other asymmetric centers or the two nitrogens are not chemically equivalent, the stereochemical possibilities increase rapidly.

Figure 6 shows the absolute configuration of (-)D-1,2-propanediamine. This has been determined to be R in two ways. It has been

![Figure 6. Absolute configuration of (-)D-1,2-propanediamine I, and R-N,N'-dimethyl-1,2-propanediamine, II.](image-url)
related to D-alanine, a compound of known absolute configuration by converting the -COOH group of alanine to the -CH₂NH₂ group in 1,2-propanediamine. This assignment was later confirmed by Saito and Iwasakis in an anomalous dispersion X-ray study on a single crystal of trans-dichlorobis(−)-1,2-propanediamine)cobalt(III) chloride hydrochloride dihydrate.

The R-N,N'-dimethyl-1,2-propanediamine was prepared from R-1,2-propanediamine by the conversion of the amine groups to methylamine groups. Thus the configuration of the asymmetric carbon in this ligand also has to be R as shown in Figure 6.

On coordination ethylenediamine and C or N substituted ethylenediamine adopt a skew or puckered conformation as a result of conformational energy requirement. Corey and Bailar were the first to do a detailed conformational analysis study of metal-ethylenediamine chelate ring system. They concluded that the chelate rings existed in enantiomeric skew or gauche conformations as shown in Figure 7. Hawkins and Buckingham, and coworkers have done a detailed conformational analysis of complexes of ethylenediamine and 1,2-propanediamine as well as N-methylethylenediamine. It was concluded that for the substituted ethylenediamine complexes, a skew conformation that allows the methylsubstituents to lie in the equatorial position is more stable. This conformational preference limits the numbers of stereoisomers that can be obtained in these systems.
Figure 7. Skew conformations of a chelated ethylenediamine: λ conformation I and δ conformation II.
EXPERIMENTAL

A. Materials

All chemicals were reagent grade unless otherwise stated. The amines, N-methylethylenediamine and N,N'-dimethylethylenediamine were purchased from the Ames Laboratories, Inc., Milford, Conn. Racemic 1,2-propanediamine (practical grade) was purchased from J. T. Baker Chemical Co. and Aldrich Chemical Co., Inc., Milwaukee, Wisc. N,N-Dimethylethylenediamine was obtained from City Chemical Corp., New York, N.Y. and 1,3-diamino-2-methylpropane was obtained from Aldrich Chemical Co., Inc. Ethylenediamine-N,N'-diacetic acid was purchased from I.G.N. Pharmaceuticals, Inc., Life Sciences Group, Plainview, N.Y. and was used without further purification. The resolving agent ammonium α-bromocamphor-β-sulfonate (NH₄BCS) was obtained from Aldrich Chemical Co. while tartaric acid was purchased from Eastman Organic Co. Optically active [Co(EDTA)]⁻ was prepared following the method of Douglas and coworkers. Ethylchloroformate was purchased from Eastman Organic Chemicals Distillation Products Industries, Rochester 3, N.Y. Lithium aluminum hydride was obtained from Foote Mineral Co., Exton, Penna. Chloroacetic acid was obtained from Aldrich Chemical Co. while deuterium oxide was purchased from Diaprep, Inc.
B. Preparation of the Ligands

1. **R-1,2-propanediamine**

   Optically inactive 1,2-propanediamine was resolved using the method of Dwyer, and coworkers\textsuperscript{28}. This involved at least ten recrystallizations of the least soluble diastereomeric salt from a mixture of the inactive ligand with D-tartaric acid and acetic acid. This R-1,2-propanediamine salt was then converted to an aqueous solution of the free ligand by the method of Bailar, and coworkers\textsuperscript{30}. This method resulted in a low yield of the free amine on distillation. In subsequent work the distillation step was omitted.

2. **R-Diethyl-1,2-propanediaminebis(carbamate)**

   The aqueous solution of R-1,2-propanediamine obtained from 100 g of its hydrogen tartrate salt (as described above) was placed in a one liter flask and methanol (300 mL) and 163 g (1.9 moles) of sodium bicarbonate was added. The mixture was cooled at 3°C in an ice bath. 205 g (1.9 moles) of ethylchloroformate was then added to the mixture (with stirring) through an addition funnel. The temperature was maintained at 3°C - 6°C during this addition. The mixture was then stirred for an additional two hours in an ice bath and then allowed to sit overnight at room temperature. The solution was then evaporated to dryness using a rotary evaporator. The resulting solid was extracted with chloroform using 2-100 mL portions. The chloroform was removed by evaporation and the resulting solid taken up in 150 mL of methanol. The solution was passed at a flow rate of 2 mL/min through a column (diameter 4.2 cm) containing 300 mL (wet volume) of cation exchange resin (Dowex-50W-X8,
100-200 mesh) in the H⁺ form. The column was rinsed with 300 mL of methanol. The combined methanol solutions were evaporated to a solid which was dissolved in 270 mL of boiling ether and then cooled to 6°C. The crystals that formed were collected and dried with CaCl₂ under reduced pressure (melting point 94.5 - 95.5°C). Additional product of similar melting point was obtained by evaporating the solvent to half volume (total yield 20 g, 0.094 mole).

3. R-N,N'-dimethyl-1,2-propanediamine

Fifty milliliters of anhydrous ether and 19 g (0.5 mole) of lithium aluminum hydride was placed in a dry one liter flask. To this stirred mixture 18.5 g (0.08 mole) of R-diethyl-1,2-propane-diaminebis(carbamate) dissolved in 550 mL of ether was added through an addition funnel. The addition was carried out over a period of 45 minutes. The resulting mixture was refluxed for 5 hours and then chilled in an ice-water bath to 10°C. Enough water, 37 g (2.05 moles) was very cautiously added dropwise with vigorous magnetic stirring to just quench the reaction (about 1.5 hr.). The ether and solid fraction were separated by filtration and the solid was extracted twice with two 200 mL portions of anhydrous ether. All the ether fractions were combined and evaporated in a rotary evaporator to about 15 mL. The liquid was then distilled collecting the fraction in the boiling range 125.5 - 129°C. (yield 4.9 g, 0.048 mole).

4. N,N'-Dimethylethylenediamine-N,N'-diacetic acid

N,N'-Dimethylethylenediamine-N,N'-diacetic acid was prepared as a barium salt by the method of Cooke and Legg. A cold solution of 41 g (1.02 moles) of sodium hydroxide in 125 mL of water was added
to a cold solution of 47.5 g (0.5 mole) of monochloroacetic acid in 35 mL of water at such a rate that the temperature did not rise above 10°C. Upon neutralization the rest of the base was added rapidly. To the stirred solution 22 g (0.25 mole) of N,N'-dimethylethylene-diamine was added over a period of 90 minutes while keeping the temperature below 45°C. After a 90 minute waiting period 65 g (0.26 mole) of barium chloride dissolved in 125 mL of boiling water was added rapidly, and the solution was shaken. The cloudy suspension of Ba(DMEDDA) which formed was heated at 60°C for 30 minutes with occasional shaking, filtered from the hot solution and washed. A second crop was obtained by evaporating the solution to half volume. The combined wet yield was purified twice by stirring it in 20 mL of water at 60°C for 10 minutes and filtered while hot. It was then washed with acetone and dried for 2.5 hours at 110°C; yield 22 g.
C. Preparation of the Complexes

The complexes were prepared by the method of Cooke and Legg. 31

Complexes of EDDA

1. trans-Ethylenediamine-N,N'-diaceto(N-methylethlenediamine)Cobalt(III) nitrate, trans-[Co(N-Meen)EDDA]NO₃ - A suspension of 6.55 g (0.05 mole) of cobalt(II) carbonate and 8.8 g (0.05 mole) of ethylenediamine-N,N'-diacetic acid in 125 mL of water was heated at 60°C with occasional stirring until carbon dioxide evolution ceased (about 20 minutes). The pink solution was filtered through a medium fritted glass filter. The residue was washed with two - 20 mL portions of hot water. To the combined filtrate and washings, 25 mL 2N nitric acid, 5 g of activated charcoal and 3.7 g (0.05 mole) of N-methylethlenediamine in 20 mL of water was added successively. The complex was then oxidized by dropwise addition of 5.5 g of 30% hydrogen peroxide with stirring. The mixture was stirred for an additional two hours and the charcoal removed by filtration. The solution volume was reduced at 45°C to 40 mL using a rotary evaporator. On cooling red-violet crystals which formed were collected. The volume was reduced to 15 mL, ethanol (5 mL) was added and the solution was allowed to stand overnight in the refrigerator (6°C). The crystals which formed were collected, washed with ethanol, acetone and air dried; combined yield of trans-[Co(N-Meen)-EDDA]NO₃ 7.5 g. Anal. Calcd. for [CoC₆H₁₀N₄O₄]NO₃: C, 29.27; H, 5.42; N, 18.97. Found: C, 29.29; H, 5.42; N, 19.02.

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2. Resolution of $\text{trans-}[\text{Co(N-Meen)EDDA}]\text{NO}_3$

This compound was resolved by adapting the method of Cooke, Legg and Douglas.\(^5\) The silver tartrate resolving agent was prepared as follows. (During this synthesis the reaction flask was shielded from light). A solution of 2 g (0.050 mole) of 98% sodium hydroxide in 10 mL of water was combined with 3.8 g (0.025 mole) of D-tartaric acid in 15 mL of water and added drop-wise to a stirred solution of 8.5 g (0.050 mole) of silver nitrate in 25 mL of water. After stirring for about 30 minutes the precipitate was allowed to settle. It was then collected, washed with five - 30 mL portions of water, acetone and air dried; yield of silver tartrate 7.6 g.

The silver tartrate was used to resolve the complex as follows: A solution of 6.25 g (0.015 mole) of $\text{trans-}[\text{Co(N-Meen)EDDA}]\text{NO}_3$ in 150 mL of water was passed at a rate of 1-2 mL/min through a column (diameter 2.8 cm) containing 200 mL (wet volume) of Dowex 1-X8 strong anion-exchange resin (50 - 100 mesh) in the chloride form. The eluted complex was collected quantitatively in a stirred suspension of 2.728 g (0.0075 mole) of silver tartrate and 1.125 g (0.075 mole) of tartaric acid in 75 mL of water. (The flask was again shielded from light). The coagulated silver chloride was removed by filtration and the filtrate reduced in volume to about 20 mL at 45°C using a rotary evaporator. On cooling, more silver chloride that formed was collected and discarded. The solution was allowed to stand overnight at room
temperature and the precipitate of (-)D-trans-[Co(N-Meen)EDDA]-
Htart that formed was collected. On cooling to 6°C after add-
ing 7 mL of ethanol additional (-)D-isomer was isolated;
combined yield of (-)D-trans-Co(N-Meen)EDDA]Htart 1.02 g
([M]$_{589}$-7510°). Further addition of 3 mL of ethanol caused an
impure sample of the (+)D-isomer which was discarded to precipi-
tate. By adding 4 mL more ethanol, the (+)D-isomer, 0.2 g was
obtained. ([M]$_{589}$+6800°)

3. Conversion of (-)D-trans-[Co(N-Meen)EDDA]Htart to (-)D-trans-
[Co(N-Meen)EDDA]ClO$_4$0.5H$_2$O - The hydrogen tartrate salt was
dissolved in minimum water. Ten drops of concentrated perchloric
acid per gram of complex was added to the solution and the per-
chlorate salt precipitated almost immediately. This was collected,
washed with water, ethanol, acetone and air dried. ([M]$_{589}$-7000°).
Anal. Calcd. for [CoC$_3$H$_8$N$_4$O$_4$]ClO$_4$0.5H$_2$O. C, 25.99; H, 5.05;

4. Conversion of (+)D-trans-[Co(N-Meen)EDDA]Htart to (+)D-trans-
[Co(N-Meen)EDDA]ClO$_4$0.5H$_2$O - The hydrogen tartrate salt was
converted to the perchlorate salt using a procedure analogous
to that used for the conversion of the (-)D-isomer as described
above. ([M]$_{589}$+6700°). Anal. Calcd. for [CoC$_3$H$_8$N$_4$O$_4$]ClO$_4$-
0.5H$_2$O: C, 25.99; H, 5.05; N, 13.48. Found: C, 25.51; H, 5.15;
N, 13.69.

5. trans-Ethylene diamine-N,N'-diacetato(N,N'-dimethylethylene-
diamine)cobalt(III) nitrate, trans-[Co(sdmeen)EDDA]NO$_3$ - The

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complex was prepared in a manner analogous to that described for \textit{trans-}[Co(N-Meen)EDDA]NO\textsubscript{3} above except that 9.83 g (0.075 mole) of cobalt(II) carbonate was used and the other reagents were scaled up accordingly. After removal of charcoal, the solution was reduced in volume to 70 mL using a rotary evaporator at 45°C. On cooling fine red-violet crystals of \textit{trans-}[Co(sdmeen)EDDA]NO\textsubscript{3} which formed were collected, washed with ethanol, acetone and air dried. More product was obtained by reducing the volume further to 50 mL. Total yield 5.6 g. Anal. Calcd. for [CoC\textsubscript{10}H\textsubscript{22}N\textsubscript{1}t\textsubscript{0}\textsuperscript{3}: C, 31.33; H, 5.74; N, 18.28. Found: C, 31.35; H, 5.98; N, 18.23.

6. Resolution of \textit{trans-}[Co(sdmeen)EDDA]NO\textsubscript{3} - The complex was resolved by a procedure similar to that described for \textit{trans-}[Co(N-Meen)EDDA]NO\textsubscript{3} above using the same mole ratios. After the coagulated silver chloride had been removed, the volume of the solution was reduced to 15 mL at 45°C using a rotary evaporator. On cooling AgC\textsubscript{2} which formed was collected and discarded. Ethanol (5 mL) was added to the solution with warming. This precipitated more silver chloride with a small amount of the desired complex which was also discarded. More ethanol (10 mL) was added to the warm solution. On cooling red crystals of (-)\textsubscript{D}-[Co(sdmeen)EDDA]H\textsubscript{tar}t which formed were collected. Further cooling to 6°C overnight in the refrigerator caused more of the (-)\textsubscript{D}-isomer to precipitate. Total yield of (-)\textsubscript{D}-isomer was 1.8 g. Addition of 2 mL more ethanol precipitated 0.5 g of the impure
(+)_D-isomer that was discarded. By adding more ethanol (4 mL) 1.3 g of the (+)_D-isomer precipitated. This was recrystallized from 60:40 ethanol-water solution.

7. Conversion of (-)_D-trans-[Co(sdmeen)EDDA]Htartrate to (-)_D-trans-[Co(sdmeen)EDDA]NO_3 - To a solution of 1 g of the hydrogen tartrate salt in minimum water was added ten drops of concentrated nitric acid. The nitrate salt which precipitated almost immediately was collected, washed with ethanol, acetone and air dried. ([M]_589-5740°). Anal. Calcd. for [CoC_10H_22N_4O_4]NO_3: C, 31.33; H, 5.74; N, 18.28. Found: C, 31.42; H, 5.87; N, 18.15.


9. trans-Ethylenediamine-N,N'-diaceto(2-methyl-1,2-propanediamine)cobalt(III) nitrate monohydrate, trans-[Co(2-Mepn)EDDA]NO_3·H_2O - The complex was prepared in a manner analogous to that used for trans-[Co(N-Meen)EDDA]NO_3 as described above using the same mole ratios. After the removal of the charcoal the volume of the solution was reduced to 65 mL at 45°C using a rotary evaporator. On cooling at room temperature the red precipitate of the desired product which deposited was collected and washed with two - 10 mL portions of ethanol, acetone and air dried.

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The ethanol wash was added to the mother liquor and the solution refrigerated overnight (6°C). The additional precipitate that formed was collected, washed with ethanol, acetone and air dried. Total yield of trans-[Co(2-Mepn)-EDDA]NO₃·H₂O, 5 g. Anal. Calcd. for [CoC₁₀H₂₂N₄O₄]NO₃H₂O; C, 29.93; H, 5.99; N, 17.46. Found: C, 29.55; H, 5.46; N, 17.21.

10. Resolution of trans-[Co(2-Mepn)EDDA]NO₃·H₂O - The complex was resolved using a procedure analogous to that described for trans-[Co(N-Meen)EDDA]NO₃ above using the same mole ratios. After the coagulated silver chloride had been removed, the solution was reduced in volume to 20 mL at 45°C using a rotary evaporator. On cooling silver chloride which precipitated was removed by filtration and the solution refrigerated overnight (6°C). Red-violet beads of (-)D-transtrans-[Co(2-Mepn)EDDA]-H₅art formed. This was collected, washed with ethanol, acetone and air dried. Yield 1.2 g of the minus isomer. ([M]₅₈₉-5680°) Anal. Calcd. for [CoC₁₀H₂₂N₄O₄]C₄H₅O₆·H₂O: C, 33.20; H, 6.13; N, 11.07. Found: C, 33.13; H, 6.25; N, 10.96.


12. Conversion of (+)D-transtrans-[Co(2-Mepn)EDDA]H₅art to (+)D-transtrans-
(Co(2-Mepn)EDDA)NO₃. Attempts to isolate the (+)₆-isomer hydrogen tartrate salt from the filtrate from section 10 was unsuccessful. To this solution which showed a plus rotation at 589 nm, was added 20 drops of concentrated nitric acid and the solution refrigerated overnight (6°C). Red crystals of (+)₆-trans-[Co(2-Mepn)EDDA]NO₃ which formed were collected, washed with ethanol, acetone and air dried. Yield 0.5 g ([M]₆₉₉ +5720°). Anal. Calcd. for [CoC₁₀H₂₂N₄O₄]NO₃: C, 31.33; H, 5.74; N, 18.28. Found: C, 31.25, H, 5.92; N, 18.26.

13. (-)₆-trans-Ethylenediamine-N,N'-diacetato-(R-N,N'-dimethyl-1,2-propanediamine)cobalt(III) perchlorate, (-)₆-trans-[Co(R-sdmepn)EDDA]ClO₄ - A suspension of 1.31 g (0.01 mole) of cobalt-(II) carbonate and 1.76 g (0.01 mole) of ethylenediamine-N,N'-diacetic acid was heated at 60°C until the carbon dioxide evolution stopped (about 20 minutes). The pink solution was filtered through a medium fritted glass filter and the residue washed with two - 5 mL portions of hot water. To the combined filtrate and washings was added successively 5 mL of 2N perchloric acid, 1 g of activated charcoal and 1.02 g (0.01 mole) of R-N,N'-dimethyl-1,2-propanediamine. The complex was oxidized by dropwise addition of 1.1 g of 30% hydrogen peroxide with stirring. The solution was stirred for an additional two hours, the charcoal removed, and the volume of the solution reduced to 25 mL at 45°C using a rotary evaporator (The bulk of
solution showed a minus rotation at 589 nm.) The solution was refrigerated overnight (6°C) and the desired product precipitated with some colorless crystals (excess ligand). The total precipitate was collected and recrystallized from water. Yield 0.25 g of \((-)_{\text{p}}\text{-trans-}[\text{Co}(\text{R-sdmepn})\text{EDDA}]\text{ClO}_4\cdot([\text{M}]_{589-4560}^\circ\text{)} \) Anal. Calcd. for [CoC\(_{11}\)H\(_{24}\)N\(_4\)O\(_4\)]C\(_2\)O\(_4\): C, 30.38; H, 5.52; N, 12.89. Found: C, 29.97; H, 5.72; N, 12.83.

14. \((+)_{\text{p}}\text{-trans-Ethylenediamine-N, N'}-\text{diacetato(R-N, N'-dimethyl-1,2-propanediamine)cobalt(III) perchlorate mono hydrogen perchlorate, \((+)_{\text{p}}\text{-trans-}[\text{Co}(\text{R-sdmepn})\text{EDDA}]\text{ClO}_4\cdot\text{HClO}_4\) – The filtrate from section 13 above was reduced to 3 mL at 45°C and allowed to cool to room temperature. Red crystals which formed were collected, washed with ethanol, acetone and air dried. \(([\text{M}]_{589+200}^\circ\text{)} \) Anal. Calcd. for [CoC\(_{11}\)H\(_{24}\)N\(_4\)O\(_4\)]ClO\(_4\)·HClO\(_4\): C, 23.91; H, 4.89; N, 10.14. Found: C, 23.65; H, 4.52; N, 10.08.

15. \(\text{trans-Ethylenediamine-N, N'}-\text{diacetato(N, N-dimethylethylene-diamine)cobalt(III) nitrate hydrate, \text{trans-[Co(udmeen)EDDA]}\cdot\text{NO}_3\cdot1.5\text{H}_2\text{O} \) The complex was prepared in a manner analogous to that described for \(\text{trans-[Co(N-Meen)EDDA]}\text{NO}_3\) using 9.83 g (0.075 mole) of cobalt(II) carbonate and the other reagents scaled up accordingly. After the charcoal had been removed the solution was reduced in volume at 45°C to 80 mL using a rotary evaporator. On cooling fine crystals of the complex began to form. The solution was refrigerated (6°C) overnight; the red-violet crystals that formed were collected, washed with ethanol, acetone and air...
Yield of trans-[Co(udmeen)EDDA]NO$_3$$\cdot$1.5H$_2$O 6.1 g Anal.
Calcd. for [CoC$_{10}$H$_{22}$N$_4$O$_4$]NO$_3$$\cdot$1.5H$_2$O: C, 29.27; H, 6.10; N, 17.07.
Found: C, 29.21; H, 5.55; N, 17.04.

16. Resolution of trans-[Co(udmeen)EDDA]NO$_3$$\cdot$1.5H$_2$O - Attempt to resolve the complex using the procedure that has been used successfully for the other complexes failed.

Complexes of DMEDDA

17. trans-N,N'-Dimethylene diamine- N,N'-diacetato-(N-methyl-ethylenediamine) nitrate dihydrate, trans-[Co(N-Meen)DMEDDA]-NO$_3$$\cdot$2H$_2$O - A mixture of 10.2 g (0.03 mole) of BaDMEDDA and 8.43 g (0.03 mole) of cobalt(II) sulfate heptahydrate in 90 mL of water was stirred at 60°C for 30 minutes. The mixture was filtered through a layer of Fuller's earth and washed with 30 mL of hot water. To the filtrate and washing were added successively 15 mL of 2N nitric acid, 3 g of activated charcoal and 2.2 g (0.03 mole) of N-methylethylenediamine. The complex was oxidized by dropwise addition of 3.3 g 30% hydrogen peroxide with stirring and the solution was then stirred for an additional two hours. The charcoal was removed by filtration and the filtrate reduced in volume at 45°C to 15 mL. Ethanol (75 mL) was then added to the solution. After refrigeration (6°C) overnight the desired product as well as some colorless crystals (excess ligand) precipitated. The precipitate was collected, added to 150 mL of ethanol and stirred for two minutes.
Most of the ligand remained suspended in the alcohol and was removed by decantation. The desired product was isolated by stirring the mixture in 150 mL of hot (50°C) ethanol for 5 minutes and then collected. It was recrystallized by dissolving it in minimum water and adding an equal volume of ethanol. Yield of trans-[Co(N-Meen)DMEDDA]NO$_3$·2H$_2$O: 1.6 g

Anal. Calcd for [CoC$_{11}$H$_{24}$N$_4$O$_4$]NO$_3$·2H$_2$O: C, 30.78; H, 6.53; N, 16.32. Found: C, 30.51; H, 6.42; N, 16.04.

18. Resolution of trans-[Co(N-Meen)DMEDDA]NO$_3$·2H$_2$O - The complex was resolved using a procedure analogous to that described above for trans-[Co(N-Meen)EDDA]NO$_3$ using 0.01 mole of the complex and the other reagents scaled down accordingly. After the coagulated silver chloride had been removed, the solution was reduced in volume at 45°C to 15 mL. The silver chloride that formed on cooling was removed and ethanol (15 mL) was added to the solution. After standing for one hour at room temperature, the precipitate that formed (principally silver chloride) was collected and discarded. The solution was allowed to stand overnight at room temperature and the red crystals of (D)trans-[Co(N-Meen)DMEDDA]H$_2$O that formed were collected, washed with ethanol, acetone and air dried. Yield 0.88 g ([M]$_{589}$+1130°). Addition of 7 mL of ethanol precipitated 1.06 g of the racemate.

19. Conversion of (D)trans-[Co(N-Meen)DMEDDA]H$_2$O to (D)trans-[Co(N-Meen)DMEDDA]Cl$_2$. The hydrogen tartrate salt

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was dissolved in minimum water. Ten drops of concentrated perchloric acid per gram of complex was added to the solution and perchlorate salt which precipitated immediately was collected, washed with ethanol, acetone and air dried. ([M]$_{589}$+1070°).

Anal. Calcld for [CoC$_{11}$H$_{24}$N$_{4}$O$_{4}$]C$_{2}$O$_{4}$: C, 30.38; H, 5.52; N, 12.89. Found: C, 30.34; H, 5.81; N, 12.99.

20. Conversion of (–)$_{D}$-trans-[Co(N-Meen)DMEDDA]H$_{4}$tartr to (–)$_{D}$-trans-[Co(N-Meen)DMEDDA]C$_{2}$O$_{4}$. To the solution from section 2 above, which showed a minus rotation after the isolation of the racemate, 12 drops of concentrated perchloric acid was added. The minus isomer which precipitated within minutes was collected, washed with ethanol, acetone and air dried. ([M]$_{589}$-1020°). Anal. Calcld for [CoC$_{11}$H$_{24}$N$_{4}$O$_{4}$]C$_{2}$O$_{4}$: C, 30.38; H, 5.52; N, 12.89. Found: C, 30.43; H, 5.81; N, 12.94.

21. trans-$N,N'$-Dimethylethlenediamine-$N,N'$-diacetato-(2-methyl-1,2-propanediamine)cobalt(III) nitrate dihydrate, trans-[Co(2-Mepn)DMEDDA]NO$_{3}$$\cdot$2H$_{2}$O - The complex was prepared by a procedure analogous to that used for trans-[Co(N-Meen)DMEDDA]-NO$_{3}$$\cdot$2H$_{2}$O as described above using the same mole ratios. After the charcoal had been removed, the volume of the solution was reduced at 45°C to 25 mL using a rotary evaporator. Ethanol (30 mL) was added to the solution which was then refrigerated (6°C) overnight. The red-violet crystals that formed were collected, washed with ethanol, acetone and air dried. Yield 4.0 g Anal. Calcld for [CoC$_{11}$H$_{24}$N$_{4}$O$_{4}$]NO$_{3}$$\cdot$2H$_{2}$O$\cdot$0.5C$_{2}$H$_{5}$OH$^{13}$: C, 33.19;

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22. Resolution of trans-[Co(2-Mepn)DMEDDA]NO₃. The complex was resolved using a procedure analogous to that described above for trans-[Co(N-Meen)DMEDDA]NO₃ using 3.6 g (0.008 mole) of the complex. The other reagents were scaled down accordingly. After the coagulated silver chloride had been removed the solution was reduced at 45°C to a volume of 15 mL using a rotary evaporator. Ethanol (5 mL) was added to the solution which was allowed to stand at room temperature for two hours. The colorless precipitate of silver chloride and tartaric acid which formed was removed and the solution reduced in volume to 10 mL and then allowed to stand overnight at room temperature. Red-violet crystal of (+)D-trans-[Co(2-Mepn)DMEDDA]H₂tart which formed were collected, washed with ethanol, acetone and air dried. Yield 0.34 g ([M]₅₈₅+4310°). Anal. Calcd for [CoC₁₂H₂₆N₄O₄]C₄H₆O₆·H₂O: C, 37.21; H, 6.49; N, 10.71. Found: C, 37.02; H, 6.49; N, 10.71. On refrigeration (6°C) additional (+)D-isomer (0.4 g) was obtained. This product contained some colorless crystals (tartaric acid) and was recrystallized before it was used further.

24. Conversion of \((-)_{\text{D}}\text{trans-}[\text{Co}(2\text{-MePN})\text{DMEDDA}]\text{Htart}\) to \((-)_{\text{D}}\text{trans-}[\text{Co}(2\text{-MePN})\text{DMEDDA}]\text{ClO}_4\). To the solution from section 6 after the isolation of the \((+)_{\text{D}}\text{-isomer}, six drops of concentrated perchloric acid was added. The perchlorate salt which precipitated immediately was collected and recrystallized from 50:50 ethanol-water solution. ([M]_{589}=4200°). Anal. Calcd for [CoC_{12}H_{26}N_{4}O_{4}]C\text{ClO}_4: C, 32.11; H, 5.80; N, 12.49. Found: C, 32.16; H, 6.03; N, 12.27.

25. \text{trans-}N,N'\text{-Dimethylethylenediamine-N,N'-diacetato-(N,N'-dimethylethylenediamine)cobalt(III) nitrate monohydrate, trans-}[\text{Co}(\text{sdmeen})\text{DMEDDA}]\text{NO}_3\cdot\text{H}_2\text{O}. - The complex was prepared by a procedure analogous to that used for \text{trans-}[\text{Co}(\text{N-Meen})\text{DMEDDA}]\text{NO}_3 as described above using 0.04 mole of the complex and the other reagents scaled down accordingly. After the charcoal had been removed, the solution was reduced in volume to 60 mL using a steam bath and 400 mL of ethanol was added to it. The precipitate of impure \text{trans-}[\text{Co}(\text{sdmeen})\text{DMEDDA}]\text{NO}_3 which formed was recrystallized six times from water. Yield 0.02 g. Anal. Calcd for [CoC_{12}H_{26}N_{4}O_{4}]\text{NO}_3\cdot\text{H}_2\text{O}: C, 33.57; H, 6.53; N, 16.32. Found: C, 33.67; H, 6.52; N, 16.33.

26. \((+)_{\text{D}}\text{trans-}N,N'\text{-Dimethylethylenediamine-N,N'-diacetato-(R-1,2-propanediamine)cobalt(III) perchlorate monohydrate, trans-}[\text{Co}(\text{R-pn})\text{DMEDDA}]\text{ClO}_4\cdot\text{H}_2\text{O}. - The complex was prepared by a method analogous to that used by Legg, Cooke and Douglas\textsuperscript{5} to prepare the EDDA analogue. A suspension of 10.2 g (0.03 mole) of BaDMEDDA and

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8.43 g (0.03 mole) of cobalt(II) sulfate in 80 mL of water was stirred at 60°C 30 minutes. The solution was filtered through a layer of Fuller's earth and the residue washed with 20 mL of hot water. To the combined filtrate and washing was added a solution of 4.41 g (0.03 mole) of R-1,2-propane-diamine dihydrochloride and 1.26 g (0.03 mole) of LiOH·H2O in 65 mL of water. After the addition of 3 g of activated charcoal, the complex was oxidized by dropwise addition of 3.3 g of 30% hydrogen peroxide and the solution was then stirred for two hours. The charcoal was removed and the volume of the solution reduced to 30 mL. To this solution was added a solution of 2.1 g sodium perchlorate monohydrate in minimum volume of ethanol. On refrigeration (6°C) overnight crystal of (+)D-trans-[Co(R-pn)DMEDDA]ClO₄ formed as an ethanol solvate. The ethanol solvate was evident from the NMR spectrum of the complex. The ethanol was removed by recrystallization from water. Yield 2.0 g ([M]₅₈⁹+878°). Anal. Calcd for [COCl₃H₂₄N₄O₄]-ClO₄·H₂O: C, 29.17; H, 5.75; N, 12.38. Found: C, 29.20; H, 6.28; N, 12.21. More product can be isolated by adding more solution of sodium perchlorate monohydrate but no fraction with a minus rotation was isolated.

27. (+)D-trans-N,N'-Dimethylethylene diamine-N,N'-diacetato(R,N,N'-dimethyl-1,2-propanediamine)cobalt(III) perchlorate monohydrate, trans-[Co(R-sdmepn)DMEDDA]ClO₄·H₂O - The complex was prepared by a procedure analogous to that used for trans-[Co(N-
Meen)DMEDEDA]NO₃ as described above except that 0.01 mole of BαDMEDEDA was used and the other reagents scaled down accordingly. In addition 2N perchloric acid was used instead of nitric acid. After the charcoal had been removed the volume of the solution was reduced to 25 mL at 45°C using a rotary evaporator. On cooling the purplish-red precipitate which formed was collected and recrystallized from water. By reducing the volume further to 10 mL 0.14 g of crude (+)-d-isomer was isolated. No (-)-D-isomer was isolated and the final filtrate showed a plus rotation. Yield of (+)-trans-[Co(R- sdmepn)DMEDEDA]ClO₄·H₂O 0.07 g ([M]+589°) Anal. Calcd for [CoC₁₃H₂₈N₄O₄]ClO₄·H₂O: C, 32.47; H, 6.24; N, 11.65. Found: C, 32.71; H, 6.30; N, 11.63.

D. Electronic Absorption Spectra

Electronic absorption spectra of the complexes were recorded at room temperature with a Cary 14 spectrophotometer using a 1 cm quartz cell. The solution concentrations were 10⁻² M for the visible region and 10⁻⁴ M for the UV region. The slit was set at program, the dynode at 2 and slit control at 20.

E. Optical Rotations

Optical rotations were measured at room temperature using a Beckman Model D.U.-2 spectrophotometer with a Keston Model D polarimeter attachment (Standard Polarimeter Co., Hackensack, New Jersey) using a 5 cm or 10 cm quartz cell and solution concentrations.
of 0.05% - 0.1%. The slit was set at 0.2 mm and the wavelength at 589 nm.

F. Circular Dichroism Spectra

Circular dichroism spectra of the complexes were recorded at room temperature using a Cary 60 spectropolarimeter with CD attachment using a 1 cm and 0.5 cm quartz cells for the visible and UV regions respectively. The solution concentrations were 0.05% - 0.1% in the visible region and 0.001% - 0.002% in the UV region. The slit was set at program. The CD data was digitized and plotted by means of computer interphasing.

G. Proton Magnetic Resonance Spectra

The proton magnetic resonance spectra of 4% - 20% of the complex in D$_2$O were recorded on a Varian Associates A-60 spectrometer. Sodium trimethylsilylpropanesulfonate was used as an internal standard. The N-deuterated samples were obtained by allowing the D$_2$O solutions to sit for several weeks or by adding a few drops of 0.01N NaOH. The acidic protons on the acetyl groups also undergo deuteration under these conditions.
RESULTS AND DISCUSSION

A. Preparations

The ligand, \(N,N'-\text{dimethyl-1,2-propanediamine}, (R-\text{sdmepn})\) can be prepared easily from \(R-1,2\)-propanediamine\(^3^4\) in two steps as summarized in equations 1 and 2. Attempt to isolate the free \(R-1,2-\)

\[
\begin{align*}
\text{NH}_2\text{CH}_2\text{CH}((\text{CH}_3))\text{NH}_2 & \xrightarrow{\text{CH}_3\text{CH}_2\text{O}_2\text{CCL}} \text{NaHCO}_3 \\
\text{CH}_3\text{CH}_2\text{O}_2\text{CNHCH}_2\text{CH}((\text{CH}_3))\text{NHCO}_2\text{CH}_2\text{CH}_3 & \quad (1) \\
\text{CH}_3\text{CH}_2\text{O}_2\text{CNHCH}_2\text{CH}((\text{CH}_3))\text{NHCO}_2\text{CH}_2\text{CH}_3 & \xrightarrow{1)\text{LiAlH}_4} \\
& \xrightarrow{2)\text{H}_2\text{O}} \\
& \text{CH}_3\text{NHCH}_2\text{CH}((\text{CH}_3))\text{NHCH}_3 \\
& \quad (2)
\end{align*}
\]

propanediamine from its aqueous solution by the method of Bailar and coworkers\(^3^0\) resulted in a poor yield of the ligand. The reaction (1) was therefore carried out using the aqueous solution and a much better yield of the ligand resulted.

The ligand BarMEDDA was prepared by the method of Cooke and Legg.\(^3^1\) This can be summarized by equations 3–5.

\[
\begin{align*}
\text{C}_2\text{CH}_2\text{CO}_2\text{H} + \text{NaOH} & \xrightarrow{<10^\circ\text{C}} \text{C}_2\text{CH}_2\text{CO}_2\text{Na} + \text{H}_2\text{O} \\
2\text{C}_2\text{CH}_2\text{CO}_2\text{Na} + \text{CH}_3\text{NHCH}_2\text{CH}_2\text{NHCH}_3 & \quad (3) \\
\text{Na}_2\text{O}_2\text{CCH}_2\text{N}((\text{CH}_3))\text{CH}_2\text{CH}_2\text{N}((\text{CH}_3))\text{CH}_2\text{CO}_2\text{Na} + \text{HCl} & \quad (4) \\
\text{Na}_2\text{O}_2\text{CCH}_2\text{N}((\text{CH}_3))\text{CH}_2\text{CH}_2\text{N}((\text{CH}_3))\text{CH}_2\text{CO}_2\text{Na} + \text{BaCl}_2 & \quad (5) \\
\text{H}_2\text{O} & \xrightarrow{100^\circ\text{C}} \text{BaMEDDA} \downarrow + 2\text{NaCl} \\
\end{align*}
\]
Tables I and II lists the complexes of the EDDA and DMEDDA

### TABLE I

Stereoisomers of trans-[Co(diamine)EDDA]$^+$

Prepared and Identified

<table>
<thead>
<tr>
<th>Stereoisomers</th>
<th>Possible</th>
<th>Identified</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(Meen)EDDA]$^+$</td>
<td>$^2b$</td>
<td>2</td>
</tr>
<tr>
<td>[Co(2-Mepn)EDDA]$^+$</td>
<td>$^2b$</td>
<td>2</td>
</tr>
<tr>
<td>[Co(sdmeen)EDDA]$^+$</td>
<td>$^2b$</td>
<td>2</td>
</tr>
<tr>
<td>[Co(udmeen)EDDA]$^+$</td>
<td>$^2b$</td>
<td>1$^c$</td>
</tr>
<tr>
<td>[Co(R-sdmepn)EDDA]$^+$</td>
<td>$^2d$</td>
<td>1$^e$</td>
</tr>
</tbody>
</table>

$^a$Assumes that the nitrogens on each chelate ring will have the same absolute configuration (R,R or S,S but not R,S or S,R). $^b$Exists as a dL pair. $^c$Attempt to resolve this failed. $^d$Two isomers arising from the δ or λ conformation of the EDDA chelate ring. $^e$This reaction is stereospecific giving only an isolable (-)$_D$ isomer.

respectively prepared in this study. The number of stereoisomers possible and actually isolated are also included in these tables.

The complexes were prepared by the method of Cooke and Legg.\(^\text{31}\)

However, due to the greater insolubilities in ethanol of the complexes prepared in this study, they were isolated from their aqueous solution rather than from their ethanolic solutions. The preparation of the EDDA complexes is summarized by equations 6 and 7, while equations 8 and 9 summarizes the preparation of DMEDDA complexes. Oxidation of the complexes was accomplished in the presence of activated carbon using hydrogen peroxide. The symbol LL represents a bidentate ligand.

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TABLE II
Stereoisomers of trans-[Co(diamine)DMEDDA]⁺
Prepared and Identified

<table>
<thead>
<tr>
<th>Stereoisomers</th>
<th>Complex Ion</th>
<th>Possibleᵃ</th>
<th>Identified</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[Co(meen)DMEDDA]⁺</td>
<td>2ᵇ</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>[Co(R-pn)DMEDDA]⁺</td>
<td>2ᶜ</td>
<td>1ᵈ</td>
</tr>
<tr>
<td></td>
<td>[Co(2-Mepn)DMEDDA]⁺</td>
<td>2ᵇ</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>[Co(sdmeen)DMEDDA]⁺</td>
<td>2ᵇ</td>
<td>1ᵉ</td>
</tr>
<tr>
<td></td>
<td>[Co(R-s institutions)DMEDDA]⁺</td>
<td>2</td>
<td>1ᵈ</td>
</tr>
</tbody>
</table>

ᵃ Assumes that the two nitrogens on each chelate ring will have the same absolute configuration (R,R or S,S, but not R,S or S,R).
ᵇ Exists as a d,l pair.
ᶜ Two isomers arising from the δ or λ conformation of the DMEDDA chelate ring.
ᵈ This reaction is stereo-specific giving only an isolable (+)p-isomer. This complex was not obtained in enough quantity for a resolution.

\[
\text{CoCO}_3 + \text{H}_2\text{EDDA} \xrightarrow{\text{H}_2\text{O}, 60^\circ\text{C}} \text{[Co(H}_2\text{O)}_2\text{EDDA]} + \text{CO}_2 + \text{H}_2\text{O} \tag{6}
\]

\[
\text{Co(H}_2\text{O)}_2\text{EDDA]} + \text{LL} \xrightarrow{\text{H}_2\text{O}, C} \text{[Co(LL)}_\text{EDDA]} \tag{7}
\]

\[
\text{CoSO}_4 + \text{BaDMEDDA} \xrightarrow{\text{H}_2\text{O}, 60^\circ\text{C}} \text{[Co(H}_2\text{O)}_2\text{DMEDDA]} + \text{BaSO}_4 \tag{8}
\]

\[
\text{[Co(H}_2\text{O)}_2\text{DMEDDA]} + \text{LL} \xrightarrow{\text{H}_2\text{O}, C} \text{[Co(LL)}_\text{DMEDDA]} \tag{9}
\]

It should be pointed out that EDDA or DMEDDA can coordinate either symmetrically (trans or α-cis) or unsymmetrically.
(cis or \( \beta \)-cis)\textsuperscript{35} as shown in Figure 9. In a normal preparation of

\begin{figure}
\centering
\includegraphics[width=\textwidth]{diagram.png}
\caption{Possible configuration of coordinated EDDA (R=H) and DMEDDA (R=CH\textsubscript{3}). The remaining two positions in this study is occupied by a bidentate ligand.}
\end{figure}

trans- (or \( \alpha \)-cis) complex \hspace{1cm} Cis (or \( \beta \)-cis) complex

these complexes only the trans- or \( \alpha \)-cis complex is isolated. Special procedure have to be followed in order to get the cis- or \( \beta \)-cis- complex in larger \textsuperscript{36,37} than trace amounts.

The bulk solution from these preparations showed no optical activity except for those in which the diamine is R-pn or R-sdmepn as was expected. In the later two cases the optical activity of the bidentate ligand results in a bulk solution that is also optically active.

Several resolving agents were tried on the racemates. Optically active [Co(EDTA)]\textsuperscript{-} and \( \alpha \)-bromocamphor-\( \Pi \)-sulfonate (BCS) salts failed to resolve the complexes. A silver salt of D-tartaric acid was used for all the resolutions. A concentrated solution of the

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complex and resolving agent was kept at room temperature or in the refrigerator (6°C) for some time to allow the less soluble isomer to crystallize out. Addition of ethanol usually resulted in the formation of an oil. The (-)$_D$-isomers were less soluble than the (+)$_D$-isomers and came out of the solution first. These (-)$_D$-isomers apparently came out optically pure since recrystallization did not increase their optical activities. In some cases it was not possible to get crystals of the (+)$_D$-isomers as a hydrogen tartrate salt because of their high solubilities. In these cases, perchloric acid was added dropwise to the solution and the hydrogen tartrate anion was converted to tartaric acid with an immediate precipitation of the (+)$_D$-isomer as a perchlorate salt. One recrystallization was usually sufficient to get an optically pure isomer. In some cases perfect mirror image curves for the d& pairs with respect to the intensity of the CD peaks was not obtained. This will be discussed further in the next section.

It should be pointed out that one cannot really be sure that an optical isomer obtained by resolution is optically pure unless a naturally occurring optical isomer is available.

The resolving agent was removed by adding concentrated nitric or perchloric acid dropwise to a solution of the complex. This resulted in the precipitation of the complex as a nitrate or perchlorate salt.

The perchlorate salts are not very soluble. As a result it was necessary to convert them to chloride salts in order to get a good NMR spectra. This was accomplished by passing a solution
of the perchlorate salts through a column containing an anion ex-
change resin in the chloride form and evaporating the eluents to
dryness. The chloride salts are extremely soluble and may absorb
moisture from the air.

B. Spectra

1. **Ultraviolet-visible Spectra**

The UV-visible spectra of the complexes was examined mainly to
ascertain their trans nature. The spectra of the trans-complexes
have two main peaks in the visible region at approximately 530 nm
and 360 nm. The peak at 530 nm has a shoulder at approximately
470 nm. This distinguishes them from the cis-complexes which lack
such a shoulder. 31,35 Both the cis and trans-complexes have one
absorption band near 210 nm in the UV region. Figure 10 shows the
visible spectra for \((-\rangle)_D^{-trans-[Co(R-sdme)n]EDDA}^{+}. This spectra
is typical for all the complexes prepared in this study. The only
difference is in the location and intensity of the maximum absorp-
tion bands. This data is summarized in Table III for all the com-
plexes.

2. **Circular Dichroism Spectra**

The CD spectra for the complexes is characterized by two bands
in the visible region near 450 nm and 535 nm. The intensity of the
band near 535 nm is usually larger than that of the band near 450 nm.
Most of the CD studies that have been done on these kind of complexes
have been restricted to their spectra in the visible region. 6,7,26,31,36,38
Figure 9. Electronic Absorption Spectra for \((-)_{\text{trans}}-[\text{Co(R-sdmpn)EDDA}]^+\)
<table>
<thead>
<tr>
<th>Complex Ion</th>
<th>Absorption</th>
<th>(\lambda\text{(nm)})</th>
<th>(\varepsilon)</th>
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<tbody>
<tr>
<td>trans-[Co(Meen)EDDA](^+)</td>
<td>526</td>
<td>104</td>
<td></td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>sh</td>
<td></td>
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<td></td>
<td>365</td>
<td>125</td>
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<td>226</td>
<td>2.27 (\times) 10(^4)</td>
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<td>trans-[Co(2-Mepn)EDDA](^+)</td>
<td>521</td>
<td>97.7</td>
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<tr>
<td></td>
<td>466</td>
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</tr>
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<td>104</td>
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<td></td>
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<td>356</td>
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<td>211</td>
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<td>460</td>
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<td></td>
<td>360</td>
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<td>380</td>
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<td>trans-[Co(R-pn)DMEDDA](^+)</td>
<td>524</td>
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<td></td>
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<tr>
<td></td>
<td>450</td>
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<td>363</td>
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<td></td>
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<td>524</td>
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<td></td>
<td>465</td>
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<td>360</td>
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<tr>
<td></td>
<td>216</td>
<td>2.37 (\times) 10(^4)</td>
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In this study we also report the CD spectra of the complexes in the UV region. In this region all the complexes have a band which has an intensity much larger than the two bands in the visible region. Figures 10-14 shows the CD spectra the visible region for some of the complexes prepared in this study. The CD data for all the complexes in both the visible and UV region are summarized in Table IV and V for the EDDA and DMEDDA complexes respectively. The complexes have three main CD bands. The two high energy bands have the same sign and the sign of the lowest energy band is opposite to this.

3. **Proton Magnetic Resonance Spectra**

Cooke and Legg\textsuperscript{31} have presented a detailed analysis of the NMR spectra for these kind of complexes.

Figures 15-24 shows the NMR spectra for the complexes prepared in this study. For the complexes that gave a $d\bar{l}$ pair, the spectra of one of the enantiomers is shown. The spectra of the other enantiomer is identical to the one shown as well as the spectra of the racemate or the unresolved complex.

The NMR spectra of these compounds are so complex that a complete assignment of all the lines cannot be made. As was shown in Figure 8, the chelate rings of the tetradentate ligand are of different types. They will be referred to as the "E-ring" (chelate ring containing the two nitrogen atoms and the "R-ring" (the acetate chelate ring). The protons associated with the R-ring are subjected to the combined deshielding effects of the carboxylate and amine groups and
Figure 10. CD Spectra for trans-[Co(sdmeen)EDDA]^+ (Spectrum I (+)_D-isomer; Spectrum II (-)_D-isomer)
Figure 11. CD Spectra for (-)$_D$-trans-[Co(R-sdmpn)EDDA]+$^+$.
Figure 12. CD Spectra for \( \text{trans-}[\text{CO(Meen)DNEDDA}]^+ \) (Structure I (+)-isomer; Structure II (-)D-isomer)
Figure 13. CD Spectra for $\text{trans-}[\text{Co(2-Mepn)DMEDDA}]^+$
(Structure I (+)$_D$-isomer, Structure II (-)$_D$-isomer)
Figure 14. CD Spectra for (+)_D^- \text{trans-}[\text{Co}(R\text{-pn})\text{DMEDDA}]^+. 

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<sup>a</sup>The (+) or (-) designation for the complexes refers to the sign of the lowest energy CD band.
### TABLE V

Circular Dichroism Data for DMEDDA Complexes

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<td></td>
<td>247</td>
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*aThe (+) or (-) designation for the complexes refer to the lowest energy CD band.*
resonate in the region 3.1 to 4.5 p.p.m. There are two kinds of N-C-C-N rings. One is a part of the tetradentate ligand and the other is the bidentate ligand. The protons associated with these two N-C-C-N rings are subjected only to the deshielding effect of the amine groups. They therefore resonate at higher field than those associated with the R-ring. These protons are found in the 2.5 to 3.5 p.p.m. region. It is seen that the R-ring proton resonances may overlap those of the N-C-C-N protons which makes it difficult to assign individual proton resonances. Moreover, when this overlap occurs, it becomes impossible to get an integration of the R-ring protons without including those protons associated with the N-C-C-N chelate rings.

There are two other protons in the complexes besides those associated with the R-ring and N-C-C-N chelate rings. The protons attached to the nitrogens exchange rapidly with the solvent and are sometimes not observed. When they are seen, they appear as very broad bands at 4.4 p.p.m. or greater since they are deshielded by the nitrogen to which they are attached. The methyl-protons are found at 2.2 to 2.8 p.p.m. for methyl group attached to nitrogen, and at 1.2 to 1.5 p.p.m. for C-methyl. Once again we can see that the N-methyl signal may overlap those of the protons associated with the N-C-C-N chelate rings. But here the problem is not as great since the N-CH₃ signal is much more intense than any signal associated with the N-C-C-N chelate ring protons. It should be pointed out that the ranges discussed above are consistent with the data that has been obtained on similar complexes by other workers.⁵,³⁶,⁴⁰,⁴¹
A more detailed assignment of the NMR spectra now follows.

If the remaining two positions in Figure 8 are taken by a symmetrical bidentate ligand such as en or sdmeen, then the two acetate rings will be identical chemical environment. However, the two protons on the acetate ring are not identical and will be referred to as $H_a$ and $H_b$ (Figure 8). $H_b$ is the proton inside the acetate ring over the E-ring and $H_a$ is outside away from the ring. In these inert complexes the conformation of the acetate ring is fixed and we get a symmetrical AB quartet due to two spin-spin coupled protons in different chemical environment. The signals due to $H_a$ are at lower field than those due to $H_b$. This type of spectrum has been observed for compounds with similar acetate rings. If the two remaining positions on the complex in Figure 8 are occupied by an unsymmetrical bidentate ligand, such as R-pn or Meen, then the two acetate rings are no longer in an identical chemical environment. This gives rise to two sets of quartets, AB and A'B' from the protons labelled $H_a$ and $H_b$ in Figure 8. The eight lines expected from this two sets of quartets are not seen in all the complexes with DMEDDA because steric interactions involving the N-methyl groups on DMEDDA apparently alter the stereochemistry so that the chemical environments of the acetate rings are similar.

These acetate ring protons are relatively acidic and will undergo proton exchange. When the complex is placed in $D_2O$ for periods of up to a week or more the signal associated with these protons disappears confirming the original assignment of these lines.

For the N-C-C-N chelate ring protons several possibilities exist. The protons associated with the E-ring (N-CH$_2$-CH$_2$-N chelate ring of the tetradentate ligand) are at considerable distances from
the bidentate ligand and therefore will probably not be affected
by the dissymmetry of this ligand. The N-C-C-N chelate ring is
puckered. The E-ring can therefore be considered to have two sets
of equivalent protons, (each set containing an axial and an equator­
ial hydrogen) irrespective of the symmetry of the bidentate ligand.
This will result in a symmetrical $A_2B_2$ pattern which theoretically
can have from 14 to 24 lines depending on the chemical shifts and
coupling constants between the axial and equatorial protons. 43

The proton associated with the bidentate ligand chelate ring
exhibits an $A_2B_2$ pattern too if the ligand is symmetrical as in en
or sdmeen. The $A_2B_2$ pattern will become an ABCD pattern when the
two nitrogen ends of the molecule are different as in Meen; an ABX
pattern when one of the protons on one carbon atom is replaced by
a methyl group as in R-pn; and an AB pattern when there are two
methyl substituents on the same carbon atom as in 2-Mepn. The
ABCD pattern can give 32 lines while the ABX system can give 10
to 12 lines. 44 The resonance lines associated with the protons of
the two N-C-C-N chelate rings overlap. When this is coupled with
the large number of lines possible for each pattern, it then be­
comes clear why it is difficult to assign each pattern. But the
protons associated with the E-ring are subjected to the extra
deshielding effect of the acetate group and will therefore be
further down field than those of the bidentate ligand. The
poorly resolved pattern observed in the 2.5 to 3.5 p.p.m. region in
these complexes can be assigned to the protons of the N-C-C-N
chelate rings since the other lines can confidently be assigned.

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There are three kinds of methyl groups in these complexes, methyl on carbon, methyl on nitrogen of the bidentate ligand and methyl on nitrogen of the tetradentate ligand.

The C-methyl group is found with the bidentate ligands R-pn, sdmepn and 2-Mepn. For all three the C-methyl proton signal appears as two lines. The two lines due to the C-methyl of R-pn and sdmepn are doublets which arise as a result of the splitting of the methyl signal by the proton on the chiral carbon. For the 2-Mepn the two lines are two singlets since the two methyl groups are not equivalent (one is axial and the other equatorial). In all cases these C-methyl group protons are found upfield in the region of 1.2 to 1.5 p.p.m., well removed from the signals of the rest of the complex. Their separation from the other signals makes their assignment relatively easy.

For the N-methyl proton signals, those associated with DMEDDA ligand are easier to assign. These protons are influenced by the combined deshielding effect of the acetate group and the nitrogen to which they are attached. As a result they must be the methyl group signals that appear furthest downfield in the region of 2.6 - 2.8 p.p.m. Even though the proton signals from the E-ring may appear in this region the methyl proton signals can still be assigned confidently because of their much greater intensity. This DMEDDA methyl proton signal is not markedly affected by substituents on the carbon atom of the bidentate ligand but can be greatly affected by substituents on the nitrogen atom of the same ligand. The N-methyl protons of DMEDDA complexes appear as a singlet at 2.66 p.p.m. when
the bidentate ligand is 2-mepn and as two closely spaced singlets at 2.66 and 2.68 p.p.m. with R-pn. However the same N-methyl protons generate two singlets separated by 10 Hz when the bidentate ligand has one N-methyl substituent as in meen. In these cases the complex is not symmetrical and one would expect the signal of the two N-methyl protons on the DMEDDA to have different chemical shifts. Apparently, the difference between the two methyl groups, when the dissymmetry is due to a substituent on the carbon atom of the bidentate ligand, is not large enough to be seen in the 60 Mc instrument used for this study.

The N-methyl protons of the bidentate ligand are not deshielded as much as the N-methyl protons of DMEDDA. The former are deshielded by only the nitrogen atom while the latter are deshielded by the acetate group in addition. Moreover, the N-methyl proton signals of the bidentate ligand appear as a doublet as a result of the coupling between them and the nitrogen proton. The nitrogen of the DMEDDA ligand does not have such a proton and hence its N-methyl proton signals appear as a singlet in all the complexes. As a result of this splitting, the N-methyl of the bidentate ligand can be assigned with confidence.

When the bidentate ligand is coordinated in the EDDA complexes the N-methyl signals of the bidentate appear in the region from 2.52 to 2.62 p.p.m. These same N-methyl protons in the DMEDDA complexes appear at higher fields (2.24-2.26 p.p.m.). This additional shielding could be due to shielding from the N-methyl bond on the DMEDDA.
or due to steric interaction between the N-methyl on the DMEDDA and the N-methyl on the bidentate forcing the bidentate N-methyl group into a partially axial environment. This steric interaction however would also be expected to influence the N-methyl signal of the DMEDDA. However, this signal is found at or near 2.67 p.p.m. for all of these complexes regardless of whether there is an N-methyl of the bidentate or not. Thus the shift of the bidentate N-methyl to higher fields must be due to DMEDDA shielding.

This methyl group on a nitrogen has additional interesting behavior. It appears as a doublet due to coupling with the N-H proton or as an apparent triplet. The apparent triplet arises as a result of exchange of the N-H proton in D₂O. On exchange the N-methyl proton signal is not split by the N-D deuterium. The apparent triplet arises because of incomplete exchange which results in the superimposition of a singlet on a doublet. On complete exchange which may take place in as short a time as ten minutes or as long as several weeks depending on the complex or the situation, the signal becomes a singlet. The exchange can be accelerated by the addition of a few drops of 0.01 N NaOH. This transformation from a doublet to an apparent triplet and to a singlet helps support the assignment of these N-methyl proton signals which are found in the 2.2-2.7 p.p.m. region.

Another behavior of this methyl group which is peculiar to the EDDA complexes is that on exchange a new signal may appear at higher field. This new signal can be assigned to the bidentate ligand N-methyl protons since the signal previously assigned to
this group decreases as the new peak grows. There was never a complete transfer of this signal to the new chemical shifts even after several months of observation. Addition of NaOH makes the exchange occur rapidly, reaching equilibrium intensities within a matter of minutes. (The new peak appears at this time and did not increase in intensity on standing). This will be discussed in more detail in Part C, Section 2.

The assignment of the NMR signals are summarized in Table VI while Figures 15-24 shows the NMR spectra for the complexes.
Figure 15. The NMR Spectrum of trang-[Co(Meen)EDDA]$^+$
A and B - Before and after H-D exchange respectively.
Figure 16. The NMR Spectrum of $\text{trans-}[\text{Co(udmeen)EDDA}]^+$
Figure 17. The NMR Spectrum of trans-[Co(sdmee)EDDA]+. A and B - Before and after H-D exchange respectively.
Figure 18. The NMR Spectrum of \textit{trans-}[\text{Co(R-sdmepn)EDDA}]^+.
Figure 19. The NMR Spectrum of trans-[Co(R-sdmepn)DNEDDA]⁺.
Figure 20. NMR Spectrum of trans-[Co(R-pn)DMEDDA]$^+$

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Figure 21. The NMR Spectrum of trans-[Co(Meen)DMEDDA]$^+$

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Figure 22. The NMR Spectrum of trans-[Co(admeen)DMEDDA]^+
Figure 23. The NMR Spectrum of trans-[Co(2-Mepn)EDDA]$^+$
A and B - Before and after H-D exchange respectively.
Figure 24. The NMR Spectrum of trans-[Co(2-Mepn)DMEDDA]^+

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<th>Assignment</th>
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*Doublets that collapses to singlets on H-D exchange
TABLE VI (Continued)

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<td><strong>Res. freq.</strong></td>
<td><strong>No. of H's</strong></td>
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</table>

* Doublets that collapses to singlets on H-D exchange
TABLE VI (Continued)

<table>
<thead>
<tr>
<th>Assignment</th>
<th>[Co(2-Mepn)EDDA]$^+$</th>
<th>[Co(2-Mepn)DMEDDA]$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Res. freq.</td>
<td>No. of H's</td>
</tr>
<tr>
<td>p.p.m.$^a$</td>
<td>p.p.m.$^a$</td>
<td></td>
</tr>
<tr>
<td>$\geq$NCH$_2$CO$_2^-$</td>
<td>4.41</td>
<td>4.8</td>
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<tr>
<td></td>
<td>4.36</td>
<td></td>
</tr>
<tr>
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<td>4.11</td>
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</tr>
<tr>
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<td>4.06</td>
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</tr>
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<td></td>
</tr>
<tr>
<td></td>
<td>3.18</td>
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<tr>
<td>$\geq$NCH$_2$CH$_2$N$_t$</td>
<td>3.34</td>
<td>5.03</td>
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<tr>
<td>$\geq$NCH$_2$CN$_t$</td>
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</tr>
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<td>CN(Ac)CH$_3$</td>
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<td></td>
</tr>
<tr>
<td>$\geq$C(CH$_3$)$_2$</td>
<td>1.40$^b$</td>
<td>6.03</td>
</tr>
<tr>
<td></td>
<td>1.32$^b$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Sodium trimethylsilylpropanesulfonate as internal standard.

$^b$ The signal at higher field is assumed to be due to axial N-methyl.

$^c$ These signals partially shifts to upfield on H-D exchange.
C. Stereochemistry and Chelate Ring Conformation

1. Stereochemical Considerations

Corey and Bailar\textsuperscript{18} have discussed the stereochemistry of N-C-C-N chelate ring in Co(III) complexes containing one or more ethylenediamine ligands and found that the N-C-C-N rings adopt either a \( \lambda \) or \( \delta \) conformation Figure 25. For complexes containing EDDA, it was assumed by Legg and Cooke\textsuperscript{31} that the ethylenediamine backbone of the tetradentate ligand is fixed with either a \( \lambda \) or \( \delta \) N-C-C-N chelate ring conformation. The bidentate ligand coordinated in the fifth and sixth position can adopt either the same ring conformation as the tetradentate ligand resulting in a complex with a \( \lambda\lambda \)- or \( \delta\delta \)- N-C-C-N chelate ring conformation, or it can adopt the opposite conformation resulting in a complex with \( \lambda\delta \)- or \( \delta\lambda \)- N-C-C-N chelate ring conformation. Corey and Bailar\textsuperscript{18} considered the various N-C-C-N ring conformations in the complex trans-[Co(en)\textsubscript{2}X\textsubscript{2}]\textsuperscript{+} and found that the arrangement where the two N-C-C-N backbones adopt the same conformation (\( \lambda\lambda \) or \( \delta\delta \)) is favored over the one where they adopt different arrangement (\( \lambda\delta \)) by an energy difference of about 1.0 kcal. The cause of this difference is the steric inter-

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure25.png}
\caption{Possible Conformation of N-C-C-N Chelate Ring.}
\end{figure}
action between the N-H protons on different ethylenediamine rings.

Corey and Bailar also discussed the orientation of the methyl group in the analogous ligand R-1,2-propanediamine. The staggered arrangement of the N-C-C-N ring allows the methyl group to be in either an equatorial or axial orientation (Figure 26). Calculations by Corey and Bailar indicate that the equatorial orientation is favored by 0.6 kcal. Hawkins calculates that the energy difference may be even greater (up to 2.8 kcal). He indicates that a distortion of the N-C-C-N ring conformation from the λ or δ arrangement would alleviate non-bonded interaction of an axial methyl group and reduce this energy difference. Comparable results have been found by other workers who have shown that methyl groups on either carbon or nitrogen atoms in similar complexes prefer an equatorial orientation.

The known orientation of groups around the asymmetric carbon atom in R-pn and R-sdmepn requires that the ring adopt a λ conformation if the C-methyl group is equatorial with respect to the N-C-C-N ring.

Legg, Cooke and Douglas have discussed the absolute configuration of the complexes of trans-[Co(en)EDDA]⁺ and trans-[Co(R-pn)EDDA]⁺.
When the EDDA coordinates the cobalt(III) such that the acetate oxygens are trans then the two configurations shown in Figure 27 are possible. The two configurations have been labelled $\Delta(C_2)$ and $\Lambda(C_2)$ respectively for Structures I and II. The $C_2$ refers to the two-fold rotation axis that passes through the center of the complex and bisects the two diamine chelate rings. When the en is replaced by R-pn, the conformation of the bidentate ligand is defined in the $\lambda$ conformation. Two structures with R-pn are possible as shown in Figure 28. The ring combinations which result are $(\lambda\lambda)$ and $(\lambda\delta)$ where
Figure 28. Diagram of $\Delta(C_2)$ and $\Delta(C_2)$ complexes using trans-
$[\text{Co(R-pn)EDDA}]$ as an example.

II, $\Delta(C_2)$–complex ($\delta\lambda$)

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the first symbol in parenthesis gives the conformation of the bidentate ligand and the second the tetradentate. Legg and coworkers have obtained both possibilities for trans-[Co(R-pn)EDDA]+ and found that unlike the results for trans-[Co(en)₂X₂]⁺ which favor the λλ possibility¹⁸, the λδ arrangement is favored by a factor of 2 to 1. The λλ arrangement resulted in a steric interaction between one of the N-H protons on the R-pn and the Ha protons on the acetate arm of EDDA. The interactions were confirmed by NMR data which placed Ha at lower field in the λλ arrangement due to the concepts of steric compression.⁴⁷ The interaction between protons on neighboring nitrogen atoms which were important in trans-[Co(en)₂X₂]⁺ are not as significant in the compounds in this study. Similar results were found by Schoenberg and coworkers with complexes of cobalt(III) with the ligand ethylenediamine-N,N'-di-L-α-propionic acid (LL-EDDP) which is analogous to EDDA except that one of the protons on each of the acetate arms has been replaced by a methyl group such that the chiral carbon always has S asymmetry. When the [Co(en)LL-EDDP]+ was separated in diastereometric forms the Δ(C₂) and Λ(C₂) compounds were obtained in comparable yields because the bidentate ligand, en, can adopt either a λ or δ conformation. When the en was replaced by either R-pn or S-pn, however, the λδ or δλ combination respectively was favored. In the case where the C-methyl group was in the Ha position (see Figure 28) directly opposite the N-H proton on R-pn, the λδ possibility was favored 10 to 1. The steric interaction between the methyl in the
H$_a$ position and the N-H on the bidentate ligand was confirmed by the NMR spectra of [Co(en)LL-EDDP]$^+$. In the $\Delta$(C$_2$)-isomer where the C-methyl was in position H$_b$ (see Figure 29) away from the bidentate ligands N-H protons, the CH$_2$-CH$_2$ NMR signal due to the en ligand was a singlet indicating that the bidentate ligand was rapidly flexing or changing from $\lambda$ to $\delta$. In the $\Lambda$(C$_2$)-isomer the C-methyl was in position H$_a$ and the en ligand exhibited a complex NMR signal. This suggests that a C-methyl in the H$_a$ position sterically interact with the bidentate ligand restricting its motion and the complex signal results. In the complexes of this study where the methyl group is on the nitrogen of the bidentate ligand a similar interaction takes place; in this case with proton H$_a$ on the acetate arm of the tetradentate. When the methyl was on the nitrogen atom of the tetradentate (as in DMEDDA) instead of the acetate carbon atom, no interaction was found between the methyl group and the N-H protons on the bidentate. Legg and Cooke$^{31}$ found that in trans-[Co(en)DMEDDA]$^+$ the methylene proton signal due to the en ligand was a singlet confirming this lack of interaction. While these assumptions are reasonable based on previous studies, without the availability of X-ray data, one cannot be certain of the orientation of the methyl in these complexes or the conformation of the chelate rings.

2. Conformation of the bidentate chelate ring -

As stated earlier, the N-C-C-N backbone of the tetradentate ligand is fixed in either the $\lambda$ or $\delta$ conformation in these complexes. It is however, not certain whether the bidentate ligand is fixed in
Legg and Cooke\textsuperscript{31} have reported a detailed NMR analysis of trans-[Co(en)EDDA]\textsuperscript{+}. In this report they assigned a sharp line at 2.87 p.p.m. in the NMR spectrum, that integrates to 4.1 protons to the methylene protons of the ethylenediamine. They concluded that the sharpness of this peak is a consequence of a rapid change of the chelate ring conformation from \(\lambda\) to \(\delta\). Similar results\textsuperscript{31} were also seen with trans-[Co(en)DMEDDA]\textsuperscript{+}. The complexes prepared in this study all contain C-methyl or N-methyl substituents on the bidentate ligand and no such intense peak was observed. This would indicate that the methylene protons on the bidentate ligand in these complexes are in different chemical environments which could indicate that they do not undergo such \(\delta-\lambda\) chelate ring conformational changes within the time constraints of the NMR. This is reasonable because in these substituted complexes such a change will put the C- or N-methyl groups that were in a favored equatorial position into a less favored axial position.

For the DMEDDA complexes which also contain substituents on the nitrogens of the bidentate ligand, such a \(\lambda-\delta\) chelate ring change is even more difficult as compared to the EDDA complexes with the same ligand. This is because there is an appreciable steric interaction between the methyl groups on the DMEDDA and the methyl groups on the bidentate. Such a \(\lambda-\delta\) flexing or conformational change will increase the steric interaction that had apparently been minimized already.
In section 2 of B above it was stated that for the EDDA complexes NMR signals arising from the N-CH$_3$ on the bidentate ring will move partially upfield of standing D$_2$O. This indicates that its chemical environment is changing. It was also observed that the change will take place immediately if NaOH is added to the D$_2$O solution and that when NaOH is used to cause the change the relative intensities of the old and new chemical shifts did not change after several months of observation.

In order to account for these observations, one might attribute them to racemization of the complex, particularly since the change in chemical shift is accelerated by the addition of NaOH. It is known that racemization in this kind of complexes is base catalyzed. A true racemization cannot be taking place because if this were the case it would have resulted in a mirror image complex and there would not have been any change in the NMR spectrum. So if racemization is taking place it has to be a partial one. That is either the nitrogens of the tetradentate ligand or the bidentate ligand are changing their configuration (R,R to S,S say) but not both.

A partial racemization involving the tetradentate ligand can be ruled out because it will involve a concerted breakage and formation of four bonds, a statistically unlikely event. Partial racemization involving the bidentate ligand is more likely. The N-H bond on the bidentate ligand can break allowing the configuration on the nitrogen to change (R to S, or S to R). This would also change the chelate ring conformation ($\lambda$ to $\delta$ or $\delta$ to $\lambda$) and the N-methyl could still remain in a favored equatorial orientation,\(^4^9\)
but the chemical shift of the N-methyl protons in the new orientation would be different from the original. Figure 29 uses sdmeen to illustrate this and shows a $\lambda 6$-complex going to $\delta 6$-complex.

![Figure 29. Partial Racemization of $\Lambda(C_2)$ isomer R=H or CH$_3$.](image)

In both cases the N-methyl of the sdmeen is in a favored equatorial orientation. But in structure II the N-methyl of the sdmeen is directly over the π cloud density of the acetate arm and should be shielded unlike the N-methyl in structure I where this N-methyl group is over the N-H bond and should be deshielded. This change from structure I to II will account for the new chemical shift. The fact that this new peak never reaches an intensity that will make the old and new chemical shift equal is probably because this transformation from structure I to II results in a complex with same N-C-C-N chelate ring conformation ($\delta 6$ or $\lambda \lambda$), an arrangement that Legg and Cooke found to be less favored in this kind of complexes.
Another simpler process which could take place is a change in the bidentate chelate ring conformation. This change which requires no bond breakage would cause an N-methyl which was originally in an equatorial position to move to an axial orientation and hence the change in chemical shift. But it was stated earlier that the chelate rings in these substituted complexes are fixed. This apparent conflict can easily be reconciled.

It is important to note that the change in chemical shift is accompanied by an exchange of N-H protons in both of the ligands. When the N-H of the tetradentate ring is broken it becomes easier for the chelate ring to change their conformation and some of them apparently do change their conformation before the N-D bond forms. When the N-D bond forms the chelate ring becomes fixed once again. It can easily be seen from molecular model that there is steric interaction between the N-methyl of the bidentate ligand and the nitrogen proton of the EDDA. This steric interaction prevents the bidentate ligand from changing its conformation. When the N-H bond of the EDDA is broken this steric restriction no longer exists and the chelate ring is free to change its conformation. (δ to λ say). On the formation of the N-D bond completing the H-D exchange the chelate ring becomes fixed again. During this process however some of the N-methyl groups are trapped in an axial conformation.

This mechanism explains not only the change in the N-methyl protons chemical shift on H-D but also why this change is peculiar.
to the EDDA complexes. For DMEDDA complexes the tetradentate ligand has two methyl groups where the EDDA had protons. These methyl groups cause even more steric interaction thereby fixing the bidentate ligand in one conformation. Since this N-methyl group is unaffected by H-D exchange, the DMEDDA complexes do not show a change in the N-methyl proton chemical shift on H-D exchange.
D. Assignment of the Absolute Configurations to the Complexes

Legg, Cooke and Douglas have summarized the assignment of the absolute configuration of complexes from a study of CD spectra. In general the CD transitions occur at the same wavelength as the electron transitions in the complex ion. A cobalt(III) complex surrounded by six ammonia ligands in an octahedral ($O_h$) ion has two electron transitions in the visible region (Figure 30). The complexes in this study with four nitrogen donor atoms and two oxygen donor atoms in trans positions have tetragonal symmetry. The expected energy level splitting in going from a cubic or octahedral complex to a tetragonal complex are shown in Figure 30. There are four possible transitions in the d-d region for tetragonal complexes. Of these, only three, $A_{1g}-E_{1g}$, $A_{1g}-A_{2g}$ and $A_{1g}-E_{2g}$ are optically active. From theoretical considerations, the first two transitions give CD bands

\[ \begin{array}{c}
1T_{2g} \\
1T_{1g} \\
1A_{1g} \\
O_h \\
\end{array} \quad \begin{array}{c}
1E_{2g} \\
1B_{2g} \\
1A_{2g} \\
1E_{1g} \\
1A_{1g} \\
\text{Tetragonal (trans)} \\
\end{array} \]

Figure 30. The energy level splitting in $O_h$ and tetragonal (trans) complex in the d-d transition region.
of opposite sign in the visible region. This has been confirmed by experiment. The activity of the $A_{1g} - E_{2g}$ is generally much less intense than the first two. In addition, CD bands have been observed in the UV region due to charge transfer bands.

The complexes prepared in this study have the general formula \text{trans-[Co(\text{LL}')EDDA]}^+ or \text{trans-[Co(R-pn)EDDA]}^+ where LL' is a bidentate ligand which may contain a chiral carbon. These complexes are similar to the three complexes \text{trans-[Co(en)EDDA]}^+ , \text{trans-[Co(en)DMEDDA]}^+ or \text{trans-[Co(R-pn)EDDA]}^+, that have been thoroughly studied.\textsuperscript{5,6} The absolute configuration of \text{(+)}\text{D–trans-[Co(en)EDDA]}^+ has been determined\textsuperscript{5} to be $\Delta(C_2)$ as shown in Structure I, Figure 28. The \text{(-)}\text{D}-isomer has the mirror image $\Lambda(C_2)$ configuration of Structure II, Figure 28. The (+) and (-) refer to the sign of the lowest energy CD band for the complex ions. The (+)-complex has a positive CD band ($\Delta\varepsilon=+4.46$) and a negative band ($\Delta\varepsilon=-1.75$) at 532 nm and 446 nm respectively.\textsuperscript{5} The CD band for (-)-complex in this same wavelengths are $-4.40$ and $+1.72$ respectively.\textsuperscript{5} Maricondi and Douglas\textsuperscript{6} found that CD band for the \text{(+)D–trans–isomer} of [Co(en)DMEDDA] is $+2.25$ at 550 nm and $-0.15$ at 370 nm and assigned this complex $\Delta(C_2)$ configuration. Legg and coworkers\textsuperscript{5} found that the CD band for (+)\text{D–} and (-)\text{D–} isomer of \text{trans-[Co(R-pn)EDDA]}^+ is $+4.63$ and $-4.53$ at 532 nm and $-1.71$ and $+1.74$ at 446 nm respectively.

The (+)\text{D–} and (-)\text{D–} isomer of the complex named above were assigned $\Delta(C_2)$ and $\Lambda(C_2)$ configurations respectively. The configuration of the N-C-C-N backbone of the tetradeutate ligand was determined\textsuperscript{31} to be $\lambda$ and $\delta$ for the $\Delta(C_2)$ and $\Lambda(C_2)$ complexes respectively.

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For the complexes trans-[Co(en)EDDA]$^+$ and trans-[Co(en)DMEDDA]$^+$ the bidentate ligand changes conformation rapidly. For trans-[Co(R-pn)EDDA] the bidentate ligand is fixed in one conformation $\lambda$ or $\delta$. Legg and coworkers$^5$ found that the arrangements that allows the two N-C-C-N backbones to adopt different conformations ($\delta\lambda$) is favored by a factor of 2 to 1 over the arrangement in which they have the same conformation ($\lambda\lambda$ or $\delta\delta$). Similar result has been observed in other complexes.$^4\text{8}$

Assignment of the absolute configuration to the new complexes is based on the comparison of their CD bands to those of the known complexes. If their CD bands are similar then they are assigned the same absolute configuration.

1. Complexes with $\Delta(C_2)$ absolute configuration$^{50}$

The complexes containing EDDA and DMEDDA differ principally by the presence of the N-methyl groups in the DMEDDA. The assignment of absolute configuration to their complexes is based on the same arguments. These complexes have positive CD band at approximately 540 nm and 550 nm, negative CD band at 450 nm and 370 nm and a very intense negative band at 220 nm and 240 nm for the EDDA and DMEDDA respectively. Following the arguments of Legg and coworkers$^5$ these isomers are assigned $\Delta(C_2)$ absolute configuration. For this assignment the N-C-C-N backbone of the tetradentate ligand is in a $\lambda$ conformation and the secondary nitrogens of the same ligand are in SS asymmetry.$^6$

The bidentate ligand may adopt either a $\lambda$ or $\delta$ conformation. For the $\Delta(C_2)$-complexes that have bidentate ligand and that contains
no symmetric carbon, the chelate ring conformation is assumed to be \( \delta \) following the results of Legg and coworkers\(^5\) with \( \text{trans-[Co(R-pn)EDDA]}^+ \). This will result in a \( \lambda \delta \)-complex, a more favored arrangement.\(^5\)

The methyl groups in the coordinated bidentates prefer equatorial orientations.\(^2,16-20\) When the bidentate ligand adopts a \( \delta \) conformation, the secondary nitrogens which it may contain must have the R configuration since this will allow the methyl groups to adopt their preferred equatorial orientation.

For the complexes that have bidentate ligands with a chiral carbon, R-pn and R-sdmeen, the preferential orientation\(^16-20\) of the C-methyl in the equatorial position forces the bidentate chelate ring to adopt a \( \lambda \) conformation. As a result the secondary nitrogens it may contain must have S configuration in order to allow the N-methyl groups to be in their preferred equatorial orientation. Figure 31 shows a diagram of the \( \Delta(C_2)\)-trans-[Co(sdmeen)EDDA]\(^+\). The structure for the other \( \Delta(C_2)\)-complex can be derived from Figure 31 except for \( (+)_D\)-trans-[Co(R-pn)DMEDDA]\(^+\) and \( (+)_D\)-trans-[Co(R-sdmeen)DMEDDA]\(^+\) both of which should have Structure I in Figure 28. These results are summarized in Table VII.

2. Complexes with \( \Lambda(C_2) \) Configuration\(^50\)

The argument used to assign absolute configuration to \( (-)_D\)-trans-[Co(LL')EDDA]\(^+\) and \( (-)_D\)-trans-[Co(LL')DMEDDA]\(^+\) is analogous to that given above. These complexes assigned \( \Lambda(C_2) \) configuration have two CD bands in the visible region. The low energy transition

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Figure 31 Diagram of the $\Delta(C_2)$-Complex Using $\text{trans-}[\text{Co(sdmee)}\text{EDDA}]$ as an example.
**TABLE VII**
Absolute Configuration of the Δ(C₂)-Complexes

<table>
<thead>
<tr>
<th>Complex Ion</th>
<th>Configuration of EDDA or DMEDDA Nitrogens (^b)</th>
<th>Configuration of the bidentate ligand nitrogens (^b)</th>
<th>Configuration of Chiral Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>(+)-trans-[Co(Meen)EDDA] (^+)</td>
<td>SS(λ)</td>
<td>R(δ)</td>
<td></td>
</tr>
<tr>
<td>(+)-trans-[Co(2-Mepn)EDDA] (^+)</td>
<td>SS(λ)</td>
<td>(δ)</td>
<td></td>
</tr>
<tr>
<td>(+)-trans-[Co(sdmeen)EDDA] (^+)</td>
<td>SS(λ)</td>
<td>R(δ)</td>
<td></td>
</tr>
<tr>
<td>(+)-trans-[Co(R-pn)DMEDDA] (^+)</td>
<td>SS(λ)</td>
<td>(λ)</td>
<td>R</td>
</tr>
<tr>
<td>(+)-trans-[Co(2-Mepn)DMEDDA] (^+)</td>
<td>SS(λ)</td>
<td>(δ)</td>
<td></td>
</tr>
<tr>
<td>(+)-trans-[Co(R-sdmepn)DMEDDA] (^+)</td>
<td>SS(λ)</td>
<td>SS(λ)</td>
<td>R</td>
</tr>
</tbody>
</table>

\(^a\) The sign (+) refers to the sign of the lowest energy CD band for the complexes.

\(^b\) The symbol in parenthesis refers to the N-C-C-N chelate ring conformation.
is a negative CD band. The other CD band in the visible region is positive as well as the very intense band in the UV region. So these complexes have CD spectra that are mirror images (shapewise) of those discussed above. The tetradentate ligand following the arguments of Legg and coworkers\(^5\) must have \(\delta\), N-C-C-N chelate ring conformation and the nitrogen centers on the same ligand must have R asymmetry. The bidentate ligands must have \(\lambda\) conformation and the secondary nitrogens they may contain must have S configuration.\(^5\) The results are summarized by Table VIII and Figure 32 shows a diagram of trans-[Co(sdmee)EDDA]\(^+\) as a representative of the \(\Lambda(C_2)\)-complexes.

It is important to realize that when the complexes of R-sdmepn were prepared only the \((-)\) isomer was obtained with EDDA and only the \((+)\) isomer was found with DMEDDA. The \((-)\) isomer has been assigned the \(\Lambda(C_2)\) absolute configuration and the \((+)\) isomer the \(\Delta(C_2)\). A study of models of each of these configurations shows that the inability to obtain the other isomer is due to steric interactions involving the N-methyl groups of the R-sdmepn. The R-sdmepn must adopt the \(\lambda\)-ring conformation for the C-methyl group to remain equatorial (Figure 25). The coordination of the EDDA in the \(\Lambda(C_2)\) conformation (Figure 32) results in minimal interaction with the N-methyl groups. When the EDDA is in the \(\Delta(C_2)\) conformation (Figure 30) on the other hand, significant interaction is found to take place in the models.

When the tetradentate is DMEDDA, molecular models show that there is considerable interaction with the N-methyl groups of the R-sdmepn when the tetradentate is in either conformation and this
Figure 32  Diagram of (-)\textsubscript{D}-trans[Co(sdmeen)EDDA]\textsuperscript{+} As a Representative of the \( \Lambda(C_2) \)-Complexes
<table>
<thead>
<tr>
<th>Complex Iona</th>
<th>Configuration of EDDA or DMEDDA nitrogensb</th>
<th>Configuration of the bidentate ligand nitrogensb</th>
<th>Configuration of chiral carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-)-trans-[Co(Meen)EDDA]⁺</td>
<td>RR (δ)</td>
<td>S (λ)</td>
<td>( R )</td>
</tr>
<tr>
<td>(-)-trans-[Co(2-Mepn)EDDA]⁺</td>
<td>RR (δ)</td>
<td>(λ)</td>
<td>( R )</td>
</tr>
<tr>
<td>(-)-trans-[Co(sdmeen)EDDA]⁺</td>
<td>RR (δ)</td>
<td>SS (λ)</td>
<td>( R )</td>
</tr>
<tr>
<td>(-)-trans-[Co(R-sdmepn)EDDA]⁺</td>
<td>RR (δ)</td>
<td>SS (λ)</td>
<td>( R )</td>
</tr>
<tr>
<td>(-)-trans-[Co(Meen)DMEDDA]⁺</td>
<td>RR (δ)</td>
<td>S (λ)</td>
<td>( R )</td>
</tr>
<tr>
<td>(-)-trans-[Co(2-Mepn)DMEDDA]⁺</td>
<td>RR (δ)</td>
<td>(λ)</td>
<td>( R )</td>
</tr>
</tbody>
</table>

\(^a\)The sign (-) refers to the sign of the lowest energy CD band.

\(^b\)The symbol in parenthesis refers to the N-C-C-N chelate ring conformation.
is confirmed by the extremely low yield of material obtained in the preparation. However, of the two possibilities, models suggest that the \( \Lambda(C_2) \) isomer would have the least steric interaction and the (+) isomer which was assigned the \( \Delta(C_2) \) configuration is the only one found. This internal consistency between the assignment of absolute configuration and the steric interactions is a further confirmation of the assignments of absolute configuration.

E. Circular Dichroism and the Hexadecadal Rule

Shellman\textsuperscript{24} and Mason\textsuperscript{23} developed the regional sign or hexadecadal rule to explain the observed optical activity in octahedral complexes. Following the arguments of Shellman, Mason has suggested that the optical activity arising due to metal d-d electron transitions of dissymmetric octahedral trans-diacidotetraamine complexes can be interpreted with a regional signed rule.

Using the hexadecadal rule of Mason, the activity of this type of complex is proposed to arise from additive perturbing effects from amine substituents that are situated out of the tetragonal plane containing the amine nitrogen atoms. This perturbation lowers the tetragonal symmetry. The regions of space above and below this place can be divided into hexadecadants in a nodal manner. The sign of each hexadecadant depicts the contribution a substituent in that region makes to the optical activity. This was shown in Figure 4 in the introduction section.

For the complexes prepared in this study we will be looking at the effect of the methyl substituents on the optical activities.
of these complexes since these are the part of the molecule that markedly stick out of the tetragonal plane and therefore are expected to make some contribution to the optical activities of these complexes. The complex \textit{trans-}[Co(en)EDDA]\textsuperscript{+} will be taken as a base complex and will be assumed to make a constant specific contribution to the activity of these complexes. For the EDDA complexes therefore, we will be concerned only with the perturbations that occur in the bidentate ligand. Figure 33 shows the regional sign rule for the \( \Lambda(C_2)\)EDDA-complexes prepared in this study. One half of the complex is shown. The other portion is occupied by the EDDA which is assumed to make a specific constant contribution to the activity in these complexes. The sign for each region in space shown in Figure 33 is

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure33.png}
\caption{Partial regional sign arrangement above the CoN\(_4\) plane for the \( A_{1g}^{-}-A_{2g}^{-} (D_{hh}) \) CD band. Carbon atoms above the plane (+Z) are represented by solid circles (\( \bullet \)) and those below the plane (-Z) are represented by open circles (\( \circ \)). The signs shown are for substituent contributions in the +Z space. Those in the -Z space are of opposite sign.}
\end{figure}

\( A_{1g}^{-}-E_g \) transitions (550 nm) the sign is opposite of that shown. For the DMEDDA complexes we should also consider the effect of the N-methyl group on DMEDDA on the optical activity. Figure 34 shows the possibilities for the \( \Lambda(C_2) \)-complex of the DMEDDA. Structure IV is for the case when the bidentate ligand is \( R\)-sdmepn (or \( R\)-pn).
Figure 34. Partial regional sign arrangement above the Co-N plane for the A1g-A2g (D4h) CD band. Carbon atom above the plane (+Z) are represented as solid (●) and those below the plane (-Z) are represented by open circles (○). The signs shown are for the substituent contribution in the +Z space. Those in the -Z space are of opposite sign.

1. **EDDA Complexes and the validity of the hexadecadal rule in the A1g-A2g CD region.**

The complex trans-[Co(en)EDDA]+ is taken as the base complex. The CD band for the isomer that has A(C2) absolute configuration (λδ-complex) in region is +1.75°. This CD intensity is due to the two coordinated secondary nitrogens of the EDDA and its two CH2 groups in δ chelate ring conformation. Legg and coworkers found that the CD band intensities for (+)D and (-)D-tran-[Co(R-pn)EDDA]+ in this region is -1.71 and +1.74 respectively, essentially the same magnitude but of opposite sign due to the diastereomeric relationship.

The (-)D-isomer has λδ N-C-C-N conformation while the (+)D-isomer
has $\lambda\lambda$ N-C-C-N conformation. In the former case the contribution of the four CH$_2$ groups are expected to cancel each other but not in the later case. Since the magnitude of the CD intensities of the two isomers are essentially the same, it can be assumed that the CH$_2$ group makes negligible contributions to the optical activities of these complexes. This assumption is in line with the observation that has been made by other workers.\textsuperscript{22,51}

We now examine the EDDA complexes prepared in this study with respect to the validity of the hexadecadal rule. One of the complexes prepared is (-)-\textit{trans-}[Co(sdmeen)EDDA]$^+$. For this complex, the CD band intensity in the $A_{1g}$-$A_{2g}$ electron transition region is +2.71. This CD intensity is due to the four coordinated secondary nitrogens, two from the EDDA and two from sdmeen. If the contribution of the two secondary nitrogens of EDDA is taken to be 1.74\textsuperscript{5} then the two asymmetric nitrogens of the sdmeen contribute the difference between +2.71 and +1.74 or 0.49 for each N-methyl. This compares favorably with a value of +0.38 found by Tiethof and Cooke\textsuperscript{51} for an N-methyl group in \textit{trans-}[Co(sdmeen)X$_2$]$^+$. The CD intensities for the other (-)\textsubscript{D}-isomers are calculated using these numbers and the results are presented in Table IX. These show a good agreement between the calculated and observed CD band intensities except for (-)-\textit{trans-}[Co(R-sdmpn)EDDA]$^+$. Similar observation was made by Tiethof.\textsuperscript{52} He attributed this deviation to the steric interaction between the C-methyl and N-methyl groups which apparently forces the chelate ring to distort placing the methyl groups slightly away from their preferred equatorial orientations.
**TABLE IX**

Calculated CD Intensities\(^a\) for \(A_{1g}-A_{2g}\) CD Band for \(\Lambda(C_2)\) EDDA Complexes

<table>
<thead>
<tr>
<th>Complex Ion(^b)</th>
<th>Expected Contribution</th>
<th>Calculated</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>((-)-trans-[Co(en)EDDA](^+)</td>
<td>2-N-CH(_2)CO(_2)-</td>
<td>+1.74</td>
<td>+1.74(^c)</td>
</tr>
<tr>
<td>((-)-trans-[Co(Meen)EDDA](^+)</td>
<td>2N-CH(_2)CO(_2)-, N-CH(_3)</td>
<td>+2.23</td>
<td>+2.25</td>
</tr>
<tr>
<td>((-)-trans-[Co(sdmeen)EDDA](^+)</td>
<td>2N-CH(_2)CO(_2)-, 2N-CH(_3)</td>
<td>+2.71</td>
<td>+2.71(^c)</td>
</tr>
<tr>
<td>((-)-trans-[Co(2-Mepn)EDDA](^+)</td>
<td>2N-CH(_2)CO(_2)-,</td>
<td>d</td>
<td>+1.74</td>
</tr>
<tr>
<td>((-)-trans-[Co(R-sdmepn)EDDA](^+)</td>
<td>2N-CH(_2)CO(_2)-, 2N-CH(_3)(^e)</td>
<td>+2.71</td>
<td>+2.41</td>
</tr>
</tbody>
</table>

\(^a\)Intensities given as \(\Delta\varepsilon\). \(^b\)Sign \((-\)\) refers to the sign of the lowest CD band for the complex. \(^c\)These values were used to calculate the others. \(^d\)Basis for calculation cannot be fully determined. \(^e\)It is assumed that the chiral carbon makes a negligible contribution to the CD band intensity.\(^{51}\)
2. **EDDA complexes and the validity of the hexadecadal rule in the $A_{2g}-E_{1g}$ CD region**

An analysis similar to the one used above can be made. The complex $(-)-\text{trans-}[\text{Co(en)EDDA}]^{+}$ is taken as the base complex. For this the CD band intensity in this region is -4.48°. For $(-)-\text{trans-}[\text{Co(sdmeen)EDDA}]^{+}$ the CD band intensity in this region is -5.22. This gives a value of -0.37 as the contribution of each N-CH$_3$ on the bidentate ligand. These values were used to calculate the expected CD band intensities for the other complexes and the results are summarized in Table X.

The results show a good agreement between the calculated and expected CD band intensities. Greatest deviation occurred in the case of $(-)-\text{trans-}[\text{Co(R-sdmepn)EDDA}]^{+}$. This deviation was also observed for this complex in the $A_{1g}-A_{2g}$ transition region and is apparently due to the same reason (part 1 above).

3. **DMEDDA complexes and the validity of the hexadecadal rule in $A_{1g}-A_{2g}$ CD region**

Here the complexes with $\Delta(C_2)$ absolute configuration are chosen. The base complex is $(+)-\text{trans-}[\text{Co(en)EDDA}]^{+}$. With the DMEDDA complexes we need to consider the perturbation due to N-methyl substituents on the tetradentate ligand as well as the bidentate ligand. Figure 35 shows the hexadecantal arrangement. To determine the contribution of the N-methyl on the tetradentate ligand in this region we compare the CD band intensity for $(+)-\text{trans-}[\text{Co(en)EDDA}]^{+}$ and $(+)-\text{trans-}[\text{Co(en)DMEDDA}]^{+}$. The value for the former is -1.75 and

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<table>
<thead>
<tr>
<th>Complex Ion</th>
<th>Expected Contribution</th>
<th>CD Intensities</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(-)-trans-[Co(en)EDDA]$^+$</td>
<td>2N-CH$_2$CO$_2^-$</td>
<td>-4.48</td>
<td>-4.48$^c$</td>
<td></td>
</tr>
<tr>
<td>(-)-trans-[Co(Meen)EDDA]$^+$</td>
<td>2N-CH$_2$CO$_2^-$, N-CH$_3$</td>
<td>-4.85</td>
<td>-4.76</td>
<td></td>
</tr>
<tr>
<td>(-)-trans-[Co(sdmeen)EDDA]$^+$</td>
<td>2N-CH$_2$CO$_2^-$, 2N-CH$_3$</td>
<td>-5.22</td>
<td>-5.22$^c$</td>
<td></td>
</tr>
<tr>
<td>(-)-trans-[Co(2-Mepn)EDDA]$^+$</td>
<td>2N-CH$_2$CO$_2^-$</td>
<td>d</td>
<td>-4.82</td>
<td></td>
</tr>
<tr>
<td>(-)-trans-[Co(R-sdmepn)EDDA]</td>
<td>2N-CH$_2$CO$_2^-$, 2N-CH$_3$</td>
<td>-5.22$^e$</td>
<td>-4.59</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Intensities given as Aε. $^b$The sign (-) refers to the sign of the lowest energy CD band. $^c$These values were used to calculate the rest. $^d$A basis for calculation could not be determined. $^e$It is assumed that CHCH$_3$ make same contribution as CH$_2$, a contribution considered negligible.
(+)-trans-[Co(en)DMEDDA]^+. The value for the former is -1.75 and the later -0.15^6 which gives a contribution of +0.80 for each N-methyl substituent on the tetradentate. It can be assumed that the contribution of each N-methyl on the bidentate ligand is -0.49 (The sign is different from the above because while the EDDA complexes discussed above have χ6- N-C-C-N conformation the (+)D isomer are expected to have the opposite conformation 6χ). These values were used to calculate the other CD band intensities and the results are summarized in Table XI. Agreement between expected and calculated CD intensities were observed only for (+)-trans-[Co(R-pn)-DMEDDA]^+. All the other complexes (except (+)-trans-[Co(2-Mepn)-DMEDDA]^+) have one or two N-Methyl groups on the bidentate ligand. Steric interaction exists between the N-methyl groups on the bidentate ligand and the tetradentate ligand. This interaction will force both N-methyl groups to move slightly away from their preferred equatorial orientation. This will make them stick up more into the hexadecadant space and consequently they will make a contribution of magnitude larger than expected. The sign of the contribution of N-methyl on the bidentate and tetradentate ligand are opposite. However the N-methyl on the DMEDDA makes a contribution which is almost twice as great in magnitude as N-methyl on the bidentate ligand (+0.80 vs. -0.49). As a result when the N-methyls on this two ligands move away from their preferred equatorial orientation, the net result is a CD band intensity that is more positive than expected as was observed in these complexes (Table XI).
<table>
<thead>
<tr>
<th>Complex Ion</th>
<th>Expected Contribution</th>
<th>CD Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>(+)-trans-[Co(en)EDDA]⁺</td>
<td>2N-CH₂CO₂⁻</td>
<td>-1.75</td>
</tr>
<tr>
<td>(+)-trans-[Co(en)DMEDDA]⁺</td>
<td>2N(CH₃)CH₂CO₂⁻</td>
<td>-0.15</td>
</tr>
<tr>
<td>(+)-trans-[Co(Meen)DMEDDA]⁺</td>
<td>2N(CH₃)CH₂CO₂⁻, N-CH₃</td>
<td>-0.65</td>
</tr>
<tr>
<td>(+)-trans-[Co(R-pn)DMEDDA]⁺</td>
<td>2N(CH₃)CH₂CO₂⁻</td>
<td>-0.15</td>
</tr>
<tr>
<td>(+)-trans-[Co(2-Mepn)DMEDDA]⁺</td>
<td>2N(CH₃)CH₂CO₂⁻</td>
<td>-0.13</td>
</tr>
<tr>
<td>(+)-trans-[Co(R-sdmpn)DMEDDA]⁺</td>
<td>2N(CH₃)CH₂CO₂⁻, 2N-CH₃</td>
<td>-0.83</td>
</tr>
</tbody>
</table>

a Intensities given as Δε. b The sign (+) refers to the sign of the lowest energy band. c These values were used to calculate the others. d It is assumed that CHCH makes same contribution as CH₂, a contribution considered negligible. e A basis for calculation could be determined.
For the complexes trans-[Co(R-pn)DMEDDA]$^+$ and trans-[Co(R-sdme pn)DMEDDA]$^+$ only the (+)$_D$-isomers were isolated. These complexes will have $\alpha\alpha$ N-C-C-N chelate ring conformations and the contribution of the N-methyl groups to the CD band intensities was deduced from Structure IV of Figure 32. The only difference is that the sign of the contribution N-methyl of the tetradentate ligand is in a negative hexadecadal space.

4. DMEDDA Complexes and the validity of the hexadecadal rule in $A_{1g}$-$E_g$ CD region

The expected CD band intensities for the $\Delta(C_2)$ complexes can be calculated in a similar manner. The complex (+)$_D$-trans-[Co(en)EDDA]$^+$ which has a CD band intensity of $+4.46^5$ in this region is taken as the base complex. For (+)$_D$-trans-[Co(en)- DMEDDA]$^+$ the CD band intensity in this region is $-2.25^6$. The difference between the two CD band intensities is $-2.21$ which implies a contribution of $-1.11$ for each N-methyl on the tetradentate ligand. The contribution of N-CH$_3$ on the bidentate ligand is assumed to be the same as for N-methyl substituents in the EDDA complex (See Section 2 above). This was calculated to be $-0.37$. Here a value of $+0.37$ is used because the bidentate ligands here are in $\delta$ rather than $\lambda$ conformation. For the (+)$_D$-trans-[Co(R-sdme pn)DMEDDA]$^+$ which is assumed to have $\alpha\alpha$ chelate ring conformation, a value of $-0.37$ is used for N-methyl substituent on the bidentate ligand. The results are summarized in Table XII.

There was not a good agreement between the calculated and
TABLE XII  
Calculated CD Intensities\textsuperscript{a} for $A_{1g}$-$E_{1g}$ CD Band for \n$\Delta(C_2)$ DMEDDA Complexes  

<table>
<thead>
<tr>
<th>Complex Ion \textsuperscript{b}</th>
<th>Expected Contribution</th>
<th>CD Intensities</th>
</tr>
</thead>
<tbody>
<tr>
<td>(+)-trans-[Co(en)EDDA]+</td>
<td>2-N-CH\textsubscript{2}CO\textsubscript{2}⁻</td>
<td>+4.46</td>
</tr>
<tr>
<td>(+)-trans-[Co(en)DMEDDA]+</td>
<td>2-N-CH\textsubscript{2}CO\textsubscript{2}⁻</td>
<td>+2.25</td>
</tr>
<tr>
<td>(+)-trans-[Co(Meen)DMEDDA]+</td>
<td>2-N(CH\textsubscript{3})CH\textsubscript{2}CO\textsubscript{2}⁻, N-CH\textsubscript{3}</td>
<td>+2.62</td>
</tr>
<tr>
<td>(+)-trans-[Co(R-pn)DMEDDA]+</td>
<td>2-N(CH\textsubscript{3})CH\textsubscript{2}CO\textsubscript{2}</td>
<td>+2.25\textsuperscript{d}</td>
</tr>
<tr>
<td>(+)-trans-[Co(2-Mepn)DMEDDA]+</td>
<td>2-N(CH\textsubscript{3})CH\textsubscript{2}CO\textsubscript{2}⁻</td>
<td>e</td>
</tr>
<tr>
<td>(+)-trans-[Co(R-sdmepn)DMEDDA]+</td>
<td>2-N(CH\textsubscript{3})CH\textsubscript{2}CO\textsubscript{2}⁻, 2N-CH\textsubscript{3}</td>
<td>+2.99\textsuperscript{d}</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Intensities given in $\Delta\epsilon$. \textsuperscript{b}The sign (+) refers to the sign of the lowest energy CD band. These values were used to calculate the others. \textsuperscript{c}It was assumed that CHCH\textsubscript{3} contributes as much as a CH\textsubscript{2} a contribution considered negligible. \textsuperscript{d}A basis for calculation could not be determined.
observed values. The calculated values were generally larger than the observed values. This is probably again due to steric interactions between the N-methyl groups which make them move slightly away from their preferred equatorial orientation. The fact that the observed CD band intensities are lower than the calculated intensities is probably due once again to the dominance of the contribution of the N-methyl groups on the tetradentate. This is expected to contribute a value of $-1.11$ as compared to $+0.37$ for N-methyl on the bidentate ligand. When this distortion occurs the N-methyl group on the tetradentate ligand contribute more than $-1.11$ (absolute) for each N-methyl and hence a CD band intensity that is less positive than expected.
SUMMARY

Two series of complexes trans-[Co(LL')EDDA]$^+$ and trans-[Co(LL')DMEDDA]$^+$, LL' = Meen, 2-Mepn, udmeen, sdmeen, R-dmepn were prepared. EDDA was reacted with cobalt(II) carbonate and the resulting solution combined with the diamine of choice. For the DMEDDA complexes the ligand DMEDDA was first prepared by adding neutralized chloroacetic acid to sdmeen and precipitating out the ligand as the barium salt. The DMEDDA complexes were prepared by reacting the barium salt first with cobalt(II) sulfate and then with the diamines listed above except udmeen. The DMEDDA complexes with R-pn were also prepared. For both series the oxidation of the Co(II) to Co(III) was accomplished by the addition of hydrogen peroxide to the solution with the dimine.

The ligand R-pn was prepared as a tartrate salt by repeated recrystallizations. The tartrate salt was used to prepare R-sdmepn by forming its carbonate followed by a reduction.

The visible spectra of the complexes was used to ascertain their trans nature.

The NMR data showed that both the tetradeutate ligand and the bidentate ligand are fixed in their conformations. The N-methyl groups in these complexes are in their equatorial orientation. During deuteration some of the bidentate ligand seem to change their conformation.
The complexes were resolved using the silver salt of D-tartaric acid. For the resolved complexes, enantiomeric pair were obtained. The complex trans-[Co(dmeen)DMEDDA]⁺ was not obtained in large enough quantity to carry out a resolution. Attempt to resolve the complex trans-[Co(sdmeen)EDDA]⁺ were successful.

Preparation using the optically active ligand R-pn and R-sdmepn were stereospecific giving only one isomer depending on whether the tetradentate ligand is EDDA or DMEDDA.

Absolute configuration to the complexes were assigned by comparing their CD spectra to those of known complexes.

The CD band intensities for the EDDA complexes in both the $A_1g-A_2g$ and $A_1g-E_{1g}$ electron transition region showed additivity confirming the hexadecadal rule. For the DMEDDA complexes the results were not as good but these complexes showed qualitative additivity in accordance with the hexadecadal rule.
REFERENCES

10. The use of $\delta$ and $\lambda$ to specify the chirality of gauche conformations of five membered diamine chelate rings conform with their use as specified by the commission on the nomenclature of Inorganic Chemistry of the International Union of Pure and Applied Chemistry.
12. The use of R and S here to describe the absolute configuration about an asymmetric tetrahedral nitrogen atom conforms with the guidelines as proposed by Cahn, et. al.13
REFERENCES (Continued)

25. It should be pointed out that the hexadecadal rule proposed by Mason23 applies strictly to trans-CoN4X2 complexes that have cylindrical symmetry about the X-Co-X axis. Even though the complexes in this study lack such cylindrical symmetry in a strict sense conclusions can still be reached as to whether or not the rule holds for them as well.
32. The bulk of this solution showed a minus rotation.
33. The ethanol solvate which was apparent from the pmr spectrum of the complex was removed by recrystallization from water. This also was apparent by the disappearance of the ethanol lines from the pmr spectrum. No further elemental analysis was carried out.
REFERENCES (Continued)


35. The designation cis and trans was used by Legg, Cooke and Douglas\textsuperscript{5,27} and referred to the relative position of the ligating oxygens in EDDA or DMEDDA. The designation $\beta$-cis and $\alpha$-cis has been used by Legg et. al.\textsuperscript{32,33} to refer to the cis and trans complexes in the earlier designations.


50. The only complexes that have this $C_2$ (two fold rotation) axis are those that have symmetric bidentate ligands such as en, sdmeen.


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