A STUDY OF ASYMMETRIC SYNTHESSES IN
COORDINATION CHEMISTRY

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A STUDY OF ASYMMETRIC SYNTHESSES IN
COORDINATION CHEMISTRY

THESIS

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By

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Acknowledgment. The financial support of this investigation by Faculty Research, the National Institutes of Health, and the Robert A. Welch Foundation is gratefully acknowledged.
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CHAPTER I

INTRODUCTION

... There is only one striking difference between vital syntheses and their laboratory counterparts. This is the fact that when a substance whose molecule displays only axial symmetry is produced by vital synthesis in a living cell, it is often found that only one of the two possible antipodal forms predominates over the other in the resulting product; whereas the synthesis of asymmetric molecules in the laboratory invariably produces the racemic modification. This pronounced difference between natural and laboratory products has intrigued stereochemists all these years.\(^1\)

Pioneer workers in the field of stereochemistry were beset by many problems, one of which was the establishment of fundamental definitions. Early in 1904 "asymmetric synthesis" gained a firm foothold in stereochemistry as a result of an unambiguous definition of the term advanced by Marckwald:

Asymmetrische Synthesen sind solche, welche aus asymmetrisch constituirten Verbindungen unter intermediärer Benutzung optisch-activer Stoffe, aber unter Vermeidung jedes analytischen Voranges, optisch-active Substanzen erzeugen.\(^2\)


\(^2\)W. Marckwald, Berichte der Deutschen Chemischen Gesellschaft, XXXVII (1904), 1369.
In coordination chemistry optical activity may arise from three basic sources: (1) configuration of optically inactive ligands about the metallic nucleus; (2) introduction of optically active molecule(s) into the compound either as a simple ion or as a coordinated ligand; and (3) production of an asymmetric atom through coordination. Any one or any combination of these sources may give rise to optical activity. Only the first two and their combination are relevant to the work discussed in this thesis.

Tris-(ethylenediamine)-cobalt(III) ion is one of the classical examples of configurational stereoisomerism. The bidentate molecules of ethylenediamine may be arranged about the hexacovalent cobalt in two ways, one being a mirror image of the other. Various methods have been used to resolve the complex ion into its antipodal forms. For example, Werner\textsuperscript{3} resolved the cation as the chloride d-tartrate by taking advantage of the fact that one of the two possible diastereoisomers is more soluble than the other. In his work Werner used silver d-tartrate to produce the two diastereoisomers from the chloride salt. His method was improved by Broomhead, Dwyer, and Hogarth\textsuperscript{4} who substituted barium d-tartrate for the silver salt. A second order asymmetric synthesis for the separation of

\textsuperscript{3}A. Werner, \textit{Ber.}, XLV (1912), 121.

one diastereoisomer was reported by Busch.\textsuperscript{5} He first prepared
the chloro d- or l-tartrate and separated the least soluble
diastereoisomer by fractional crystallization. Then utilizing
the fact that electron transfer between Co\textsuperscript{3+} and Co\textsuperscript{4+} is rapid
and essentially first order in each of these ions,\textsuperscript{6} he added a
catalytic amount of \([\text{Co} (\text{en})_3]^{+2}\) to racemize the diastereoisomer
remaining in solution. (Hexacovalent complexes of Co\textsuperscript{4+}
have no configurational stability.) Again the least soluble
diastereoisomer was separated and the process repeated.

When optically active molecules are incorporated into the
coordination sphere of a metal ion, they often exert an in-
fluence on the configuration of the resulting complex in
addition to imparting their own optical activity. Since the
platinum-l-propylenediamine (l-pn) system has received almost
exhaustive investigation, it affords a convenient example.
Tschugaeff and Sokoloff\textsuperscript{7} reported the molecular rotations of
\([\text{Pt} (\text{en}) (1-\text{pn})]\text{Cl}_2\) and \([\text{Pt} (1-\text{pn})_2]\text{Cl}_2\) to be +96.28 and +192.0\degree
respectively, each molecule of l-propylenediamine contributing
96\degree. A third molecule should then increase the molecular
rotation to a maximum value of +288\degree at the sodium D-line.

\textsuperscript{5}D. H. Busch, \textit{Journal of the American Chemical Society},
LXXVII (1955), 2747.

\textsuperscript{6}C. D. Coryell, J. W. Irvine, Jr., and W. B. Lewis,
\textit{Journal of the Chemical Society}, Special Supplement (1949),
p. 386.

\textsuperscript{7}W. Sokoloff and L. Tschugaeff, \textit{Ber.}, XL (1907), 3464.
However, when Smirnoff\textsuperscript{8} analyzed $\left[\text{Pt}\left(1\text{-pn}\right)_3\right]\text{Cl}_4$ he found that the compound had a molecular rotation of $+1011^\circ$. Since the three molecules of base could contribute at most $288^\circ$, the remainder of the rotation must be attributed to a preferred configuration of the ligands about the platinum nucleus. He further demonstrated that there could be no stable complexes of platinum (IV) which contained three optically active, bidentate ligands, one of which was d and the other two l or vice versa. He found that only $\left[\text{Pt}\left(1\text{-pn}\right)_3\right]^{+4}$ and $\left[\text{Pt}\left(d\text{-pn}\right)_3\right]^{+4}$ were stable enough to be isolated.

Further work by Bailar, McReynolds, and O'Brien has indicated that two optically active ligands also exert some influence on the configurations of ligands about Co\textsuperscript{3+}. They reacted cis- and trans-$\left[\text{Co}\left(1\text{-pn}\right)_2\text{Cl}_2\right]\text{Cl}$ with potassium thiocyanate, aqueous ammonia, and anhydrous ammonia. When they compared the rotatory dispersion curves for the starting complexes with those of the products — the 1-propylenediamine molecules still intact, each of the products showed a trans configuration regardless of which geometric isomer was used as a starting material.


Turning to the remaining problem, Bailar, Huffman, and Jonassen$^{10}$ effected the first asymmetric synthesis in coordination chemistry in which an optically active molecule was attached as a ligand in the intermediate. They made DL-$[\text{Co(en)}_2(d\text{-tartrato})\text{Br}]$ from a direct stoichiometric reaction of $[\text{Co(en)}_2\text{CO}_3]\text{Br}$ with dextro tartaric acid and then treated the tartrato complex with ethylenediamine to obtain $[\text{Co(en)}_3]^3$$^3$ enriched in the D isomer. The intermediate complex had a rotation of $-0.19^\circ$ (at the sodium D-line), which led them to conclude that of the two isomers, $D-[\text{Co(en)}_2(d\text{-tartrato})]^+$ and $L-[\text{Co(en)}_2(d\text{-tartrato})]^+$, $L-[\text{Co(en)}_2(d\text{-tartrato})]^+$ was more abundant and hence more stable. On the other hand, the unstable $D-[\text{Co(en)}_2(d\text{-tartrato})]^+$ was more reactive and gave rise to the dextro rotatory product. From this work they also concluded that one molecule of an optically active, bidentate ligand had some tendency toward the formation of preferred configurations about the metal nucleus, but not enough to fix them.

There are several purposes which initiated this investigation. Since only one example of an asymmetric synthesis which involved an intermediate containing an optically active ligand has been reported$^{10}$, two questions immediately arise: "Is this type of asymmetric synthesis an isolated example, or

is it a stepping stone toward a generalized trend for Co (III) which may be extended to include levo rotatory, as well as dextro rotatory molecules?" In addition, asymmetric synthesis affords a new avenue for synthesizing resolved neutral complexes. The process is somewhat complicated by the fact that commonly used optically active ligands such as d- or l-propylenediamine are not easily removed once they are chelated. The problem then becomes one of finding optically active, bidentate ligands which may be easily replaced by such ligands as acetylacetone. Since the amino acids are potentially useful in this respect, preliminary investigations were designed to examine the ease with which they could be displaced from \([\text{Co(en)}_2(\text{amino acid})]\text{Cl}_2\) complexes by ethylenediamine and the effects that they exerted on the configurations of the resulting \([\text{Co(en)}_3]^+\).
CHAPTER II

EXPERIMENTAL

Preparation and Reaction of \([\text{Co(en)}_2(\text{L-aspartato})]\text{Cl}_2\)

To 10-g. of trans-\([\text{Co(en)}_2\text{Cl}_2]\text{Cl}\) dissolved in a minimum quantity of water was added 4.67-g. of L-aspartic acid. This mixture was placed in a 250-ml. round-bottomed flask which was equipped with a reflux condenser and a magnetic stirring bar. The mixture was refluxed with vigorous stirring for 1-hr.; then the purple solution was transferred to a 150-ml. beaker and evaporated to dryness in a forced-draft oven. The resulting dull purple, hygroscopic complex was then pulverized and analyzed. A 0.1-% solution of the complex had an observed rotation of \(-0.089^\circ\) at the sodium D-line.

Anal. Calcd. for \([\text{Co(en)}_2(\text{L-aspartato})]\text{Cl}_2\): Co, 15.45; eq. wt., 381.9. Found: Co, 15.29; eq. wt., 394.7.

Two grams of \([\text{Co(en)}_2(\text{L-aspartato})]\text{Cl}_2\) was placed in a 50-ml. volumetric flask. Then 5-ml. of water and 10-ml. of 56-% ethylenediamine were added. After the mixture was shaken for 1-hr. at room temperature (25°C), it was cooled to 0°C and treated with an excess of saturated KBr solution. The precipitated \([\text{Co(en)}_3]\text{Br}_3\) was filtered off, recrystallized from water, and finally washed with 95-% ethanol, acetone, and
ether. A 0.5-\% solution of the purified salt had an observed optical rotation of +0.052° at the sodium D-line.

Preparation and Reaction of \(\text{[Co(en)\(_2\)(L-glutamato)\]}\text{Cl\(_2\)}\)

Five grams of trans-\(\text{[Co(en)\(_2\)Cl\(_2\]}\text{Cl}, 2.58-\text{g. of L-glutamic acid, and 50-ml. of water were placed in a 250-ml. round-bottomed flask equipped with a magnetic stirrer and a reflux condenser. After the mixture was stirred under reflux for 1-hr., it was transferred to a 250-ml. beaker and evaporated nearly to dryness in a current of air. Then the purple glass was desiccated over CaCl\(_2\) for approximately three weeks. A dilute solution of the dull purple complex was quite acidic toward NaHCO\(_3\), and Hydriod paper indicated a pH of 2-3. This is an indication that the amino acid has chelated through the amine and only one carboxyl function. A 0.1-\% solution of the complex had an observed optical rotation of -0.129° at the sodium D-line.

\text{Anal. Calcd. for [Co(en)\(_2\)(L-glutamato)]Cl\(_2\): Co, 14.90; eq. wt., 396.0. Found: Co, 14.80; eq. wt., 401.9.}

Two grams of \(\text{[Co(en)\(_2\)(L-glutamato)]Cl\(_2\)}\) was placed in a 50-ml. volumetric flask with 5-ml. of water and 10-ml. of 56-\% ethylenediamine. This solution was placed on a shaker for 1-hr. at room temperature (25°C). The reaction products were transferred to a 150-ml. beaker, chilled in an ice bath, and treated with an excess of saturated KBr solution. The \(\text{[Co(en)\(_3\)]Br\(_3\)}\) was filtered from the solution, recrystallized
from water, and washed with 95-% ethanol, acetone, and finally ether. A 0.5-% solution of the purified salt had an observed rotation of +0.040° at the sodium D-line.

Preparation and Reaction of [Co(en)$_2$(L-leucinato)]Cl$_2$

A mixture of 4.6-g. of L-leucine, 125-ml. of water, and 10-g. of trans-[Co(en)$_2$Cl$_2$]Cl was placed in a 300-ml. round bottomed flask equipped with a magnetic stirring bar and a reflux condenser. The mixture was stirred and refluxed for 1-hr. The deep purple solution was transferred to a 250-ml. beaker and evaporated nearly to dryness in a current of air, then to dryness in a forced-draft oven at 110°C. The purple-violet [Co(en)$_2$(L-leucinato)]Cl$_2$ was pulverized and analyzed. A 0.1-% solution of the complex had an observed rotation of -0.115° at the sodium D-line.

Anal. Calcd. for [Co(en)$_2$(L-leucinato)]Cl$_2$: Co, 15.59; N, 18.4. Found: Co, 15.63; N, 18.5.

Five grams of the complex was dissolved in just enough water to effect solution and then added to 15-ml. of 56-% ethylenediamine. This solution was placed on a shaker for 1-hr. at room temperature (25°C). The resulting solution was cooled to 0°C and an excess of saturated KBr solution added to precipitate [Co(en)$_3$]Br$_3$. The salt was recrystallized from water and washed with 95-% ethanol, acetone, and ether.

Two and one half grams of [Co(en)$_2$(L-leucinato)]Cl$_2$, 5-ml. of water, and 10-ml. of 56-% ethylenediamine were placed
in a 100-ml. round-bottomed flask which was equipped with an air-driven stirrer. The flask was immersed in a water bath at $35 \pm 0.1^\circ C$, and the solution was stirred vigorously for 1-hr. Then the $[\text{Co(en)}_3]\text{Br}_3$ was precipitated and purified as described in the procedure for the $25^\circ C$ run. Identical runs were made for temperatures of $45.0 \pm 0.1$ and $55.0 \pm 0.1^\circ C$. Each of the four $[\text{Co(en)}_3]\text{Br}_3$ products was analyzed for optical activity at the sodium D-line. All concentrations were 0.5-% except for the $25^\circ C$ run which was 0.3-%.

**TABLE I**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$\alpha_D$</th>
</tr>
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<tbody>
<tr>
<td>$25^\circ C$</td>
<td>-0.066°</td>
</tr>
<tr>
<td>$35.0^\circ C$</td>
<td>-0.034</td>
</tr>
<tr>
<td>$45.0^\circ C$</td>
<td>-0.053</td>
</tr>
<tr>
<td>$55.0^\circ C$</td>
<td>-0.041°</td>
</tr>
</tbody>
</table>

*Latter three temperatures controlled to $\pm 0.1^\circ C$.*

Preparation and Reaction of $[\text{Co(en)}_2(L-lysinato)]\text{Cl}_2$

L-Lysine monohydrochloride (3.19-g.) was added to a solution of 5-g. of trans-$[\text{Co(en)}_2\text{Cl}_2]\text{Cl}$ in 75-ml. of water in a 250-ml. round-bottomed flask which was equipped with a magnetic stirring bar and a reflux condenser. The mixture was stirred and refluxed for 1-hr., transferred to a 150-ml. beaker and evaporated by a current of air. After three weeks'
desiccation over CaCl₂ the purple, hygroscopic complex was analyzed. A 0.1-% solution had an observed rotation of -0.064° at the sodium D-line.

Anal. Calcd. for [Co(en)₂(L-lysinoato)]Cl₂: Co, 14.93; N, 21.28. Calcd. for the 3.5 hydrate: Co, 12.87; N, 18.20. Found: Co, 12.91; N, 18.06. Although both the Co and N analyses are low, the Co:N ratios are nearly identical: calculated, 0.702, and actual, 0.713. These low analyses could be accounted for by 3.5 waters of hydration.

Two grams of [Co(en)₂(L-lysinoato)]Cl₂ was mixed with 5-ml. of water and 10-ml. of 56-% ethylenediamine in a 50-ml. volumetric flask and placed on a shaker for 1-hr. at room temperature (25°C). Then the solution was transferred to a 50-ml. beaker, cooled to 0°C, and treated with an excess of saturated KBr solution. Orange crystals of [Co(en)₃]Br₃ were filtered from the solution, recrystallized from water, and washed with 95-% ethanol, acetone, and ether. Optical rotation at the sodium D-line was observed to be +0.050° for a 0.5-% solution.

Preparation and Reaction of [Co(en)₂(L-malato)]Br

Ten grams of [Co(en)₂CO₃]Br was dissolved in 50-ml. of hot water, and then 4.2-g. of L-malic acid was added in small portions. When evolution of CO₂ stopped, the solution was evaporated to dryness in a forced-draft oven at 110°C to insure completeness of reaction. Since the dried product
forms a glass with water, it could not be recrystallized. The pink-red, hygroscopic mass\(^1\) was pulverized and analyzed. A 0.1-\% solution of the complex had an observed rotation of +0.180\(^0\) at the sodium D-line.

**Anal.** Calcd. for \([\text{Co}(en)\text{2}(L\text{-malato})]\text{Br}\): Co, 15.10; N, 14.34. Found: Co, 15.28; N, 14.18.

Five grams of \([\text{Co}(en)\text{2}(L\text{-malato})]\text{Br}\) was placed in a 250-ml. glass stoppered Erlenmeyer flask, and enough water was added to dissolve the complex. Twenty milliliters of 56-\% ethylenediamine was added and the resulting solution placed on a shaker for 1-hr. at room temperature (25\(^0\)). Then the solution was transferred to a 250-ml. beaker, chilled in an ice bath, and treated with an excess of saturated KBr solution. The \([\text{Co}(en)\text{3}]\text{Br}\text{3}\) which separated was recrystallized from water and washed successively with 95-\% ethanol, acetone, and ether.

Two grams of \([\text{Co}(en)\text{2}(L\text{-malato})]\text{Br}\), 5-ml. of water, and 10-ml. of ethylenediamine were placed in a 100-ml. round-bottomed flask equipped with an air-driven stirrer. The flask was immersed in a water bath at 35.0±0.1\(^0\)C and stirred vigorously for 1-hr. Isolation of \([\text{Co}(en)\text{3}]\text{Br}\text{3}\) was effected as above. Identical runs were made at 45.0 and 55.0±0.1\(^0\)C

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to examine the effects of temperature upon the optical activity of the \([\text{Co(en)}_3]^3\) formed. Observed rotations are shown below in Table II for 0.5-% solutions at the sodium D-line.

**TABLE II**

**EFFECTS OF REACTION TEMPERATURE ON THE OPTICAL PURITY OF \([\text{Co(en)}_3]\text{Br}_3\) FROM \([\text{Co(en)}_2(\text{L-malato})]\text{Br}\)**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>(\alpha_D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°C</td>
<td>-0.040°</td>
</tr>
<tr>
<td>35.0°C</td>
<td>-0.052°</td>
</tr>
<tr>
<td>45.0°C</td>
<td>-0.041°</td>
</tr>
<tr>
<td>55.0°C</td>
<td>-0.040°</td>
</tr>
</tbody>
</table>

* Latter three temperatures controlled to ±0.1°C.

Preparation and Reaction of \([\text{Co(en)}_2(\text{L-methionato})]\text{Cl}_2\)

A mixture of 10-g. of trans-\([\text{Co(en)}_2\text{Cl}_2]\)Cl, 5.24-g. of L-methionine, and 100-ml. of water was placed in a 300-ml. round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser. This mixture was refluxed for 1-hr. and then evaporated to dryness in a forced-draft oven at 110°C. The dull, gray-purple mass was pulverized and analyzed. A 0.1-% solution of the complex had an observed rotation of -0.051° at the sodium D-line.

*Anal. Calcd. for \([\text{Co(en)}_2(\text{L-methionato})]\text{Cl}_2\): Co, 14.70; N, 17.60. Calcd. for \([\text{Co(en)}_2(\text{L-methionato})]\text{Cl}_2\cdot3\text{H}_2\text{O}\): Co, 13.04; N, 15.48. Found: Co, 13.14; N, 15.06. Although three waters of hydration are required to account for the low analyses, the calculated and the actual Co:N ratios are 0.835 and 0.873 respectively.*
Two grams of the complex were mixed with 5-ml. of water and 10-ml. of 56-% ethylenediamine in a 50-ml. volumetric flask. The mixture was placed on a shaker for 1-hr. at room temperature (25°C), transferred to a 150-ml. beaker, and treated with an excess of saturated KBr to precipitate \([\text{Co(en)}_3\text{Br}_3]\). After being recrystallized from water, the product was washed with 95-% ethanol, acetone, and ether. A 0.5-% solution of the purified salt had an observed rotation of \(-0.038\) at the sodium D-line.

Preparation and Reaction of \([\text{Co(en)}_2(\text{D-tartrato})\text{Br} \cdot 2\text{H}_2\text{O}]\)

Ten grams of \([\text{Co(en)}_2\text{CO}_3]\text{Br}\) was placed in a 250-ml. beaker with 50-ml. of hot water, and 5.26-g. of D-tartaric acid was added slowly. The beaker was covered with a watch glass and left in a forced-draft oven at 110°C overnight. The dull, red-violet complex was pulverized and then analyzed. A 0.1-% solution of the complex had an observed rotation of \(-0.160°\) at the sodium D-line.

**Anal.** Calcd. for \([\text{Co(en)}_2(\text{D-tartrato})\text{Br} \cdot 2\text{H}_2\text{O}]\): Co, 13.30; N, 12.64. Found: Co, 13.25; N, 12.52.

Two grams of \([\text{Co(en)}_2(\text{D-tartrato})\text{Br} \cdot 2\text{H}_2\text{O}]\), 5-ml. of water, and 10-ml. of 56-% ethylenediamine were mixed in a 50-ml. volumetric flask and placed on a shaker for 1-hr. Identical quantities of reactants were placed in 100-ml. round-bottomed flasks equipped with air stirrers for runs at 35.0, 45.0, and
55.0±0.1°C. Rotations at the sodium D-line for 0.5-% solutions were as follows.

**TABLE III**

**EFFECTS OF REACTION TEMPERATURE ON THE OPTICAL PURITY OF**
**[Co(en)₃]⁺³ FROM [Co(en)₂(D-tartrato)]Br·2H₂O**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>α_\text{D}</th>
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<tr>
<td>35.0°C</td>
<td>+0.041°</td>
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<tr>
<td>45.0°C</td>
<td>+0.040°</td>
</tr>
<tr>
<td>55.0°C</td>
<td>+0.056°</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>Compound</th>
<th>c*</th>
<th>α**</th>
<th>$[\alpha]_{25}^D$</th>
<th>$[\eta]$</th>
<th>[Co(en)$_3$]Br$_3$ from complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(en)$_2$(L-aspartato)]Cl$_2$</td>
<td>0.1-%</td>
<td>-0.089°</td>
<td>-83.1°</td>
<td>-317°</td>
<td>0.5-% +0.052° +10.4° +49.8°</td>
</tr>
<tr>
<td>[Co(en)$_2$(L-glutamato)]Cl$_2$</td>
<td>.1</td>
<td>-.129</td>
<td>-115</td>
<td>-454</td>
<td>.5 + .040 + 8.0 + 38.3</td>
</tr>
<tr>
<td>[Co(en)$_2$(L-leucinato)]Cl$_2$</td>
<td>.1</td>
<td>-.115</td>
<td>-103</td>
<td>-400</td>
<td>.3 + .066 +27.5 +105</td>
</tr>
<tr>
<td>[Co(en)$_2$(L-lysinoato)]Cl$_2$</td>
<td>.1</td>
<td>-.064</td>
<td>-54.5</td>
<td>-215</td>
<td>.5 + .048 + 9.5 +45.5</td>
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<tr>
<td>[Co(en)$_2$(L-malato)]Br</td>
<td>.1</td>
<td>+.180</td>
<td>+177</td>
<td>+693</td>
<td>.5 - .040 - 8.0 -38.3</td>
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<tr>
<td>[Co(en)$_2$(L-methionato)]Cl$_2$</td>
<td>.1</td>
<td>-.051</td>
<td>-51.0</td>
<td>-203</td>
<td>.5 - .038 - 7.6 -36.4</td>
</tr>
<tr>
<td>[Co(en)$_2$(L-tartrato)]Br</td>
<td>0.1-%</td>
<td>-0.170°</td>
<td>-170°</td>
<td>-692°</td>
<td>0.4-% +0.021° + 5.7° +27.2°</td>
</tr>
</tbody>
</table>

*, concentration.

**, observed rotation.
CHAPTER III
DISCUSSION

Only the malato and the tartrato complexes listed in Table IV have been reported in the literature. In one of a series of articles on complex metal ammnes Duff\textsuperscript{1} reported that malic acid reacted with $[\text{Co(en)}_2\text{O}_3]X$ to give a red glass which could not be crystallized. When he evaporated the glass to dryness, he found that the amorphous powder analyzed as $[\text{Co(en)}_2(\text{malato})]X$. Bailar, Huffman, and Jonassen\textsuperscript{2} prepared their d-tartrato complex by the same method. The strained, seven-membered chelate rings in both of the complexes most probably account for their glass-like properties. The remaining compounds, all amino acid complexes, are described in this thesis. In each case the amino acid was reacted with an aqueous solution of trans-$[\text{Co(en)}_2\text{Cl}_2]\text{Cl}$. Since the initial complex is incapable of exhibiting any optical rotation, the fact that the amino acid complexes have high negative rotations indicates that the optically active amino acids might induce a preferential levo configuration about the cobalt nucleus. Assuming that each optically active ligand contributes a rotation equivalent to that of the free amino acid, one can infer the actual extent of the configurational rotation from Table V.

\textsuperscript{1}Bailar, Huffman, and Jonassen, op. cit.
\textsuperscript{2}Duff, op. cit.
TABLE V

COMPARISON OF THE SPECIFIC ROTATIONS OF CERTAIN ORGANIC ACIDS WITH THEIR COMPLEXES OF THE TYPE \([\text{Co(en)}_2(\text{acid})]^+\) or ++

<table>
<thead>
<tr>
<th>Free Acid</th>
<th>([\alpha]_D^{t3})</th>
<th>Complex</th>
<th>([\alpha]_D^{25*})</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-aspartic acid</td>
<td>+4.7°</td>
<td>([\text{Co(en)}_2(\text{L-aspartato})\text{Cl}_2])</td>
<td>-8.48°</td>
</tr>
<tr>
<td>L-glutamic acid</td>
<td>+11.5</td>
<td>([\text{Co(en)}_2(\text{L-glutamato})\text{Cl}_2])</td>
<td>-115</td>
</tr>
<tr>
<td>L-leucine</td>
<td>-10.8</td>
<td>([\text{Co(en)}_2(\text{L-leucinato})\text{Cl}_2])</td>
<td>-103</td>
</tr>
<tr>
<td>L-lysine</td>
<td>+14.6</td>
<td>([\text{Co(en)}_2(\text{L-lysino})\text{Cl}_2])</td>
<td>-7.52</td>
</tr>
<tr>
<td>L-malic acid</td>
<td>-3.4°*</td>
<td>([\text{Co(en)}_2(\text{L-malato})\text{Br})</td>
<td>+177</td>
</tr>
<tr>
<td>L-methionine</td>
<td>-8.1</td>
<td>([\text{Co(en)}_2(\text{L-methionato})\text{Cl}_2])</td>
<td>-5.10</td>
</tr>
<tr>
<td>D-tartaric acid</td>
<td>+13.5°*</td>
<td>([\text{Co(en)}_2(\text{D-tartarato})\text{Br})</td>
<td>-170°</td>
</tr>
</tbody>
</table>

*Specific rotations determined in this laboratory.

Each of the complexes investigated gave rise to an optically active tris-(ethylenediamine)-cobalt(III) bromide when treated with an excess of ethylenediamine and precipitated with saturated potassium bromide. These examples serve to illustrate that asymmetric syntheses are generally characteristic of the cobalt-bis-(ethylenediamine) series of compounds in which the third bidentate ligand is optically active. Furthermore, the trend appears to be generally applicable to the coordination compounds of Co(III).

注: Handboook of Chemistry and Physics, 40th edition (Cleveland), pp. 1752-1753.
All of the optically active amino acids which were employed as intermediate ligands were quite readily displaced from their coordinated positions by ethylenediamine. In each instance the reactions gave nearly quantitative yields of tris-(ethylenediamine)-cobalt(III) ion after one hour's shaking at 25°C. The specific rotations of the products were fairly uniform in magnitude for each reaction with the exception of the L-leucinato complex, which had a comparatively high value. Consequently the optically active amino acid ligands may be utilized in intermediate complexes leading to a resolved antipode of a neutral complex such as tris-(acetylacetonato)-cobalt(III). However, caution must be exercised to neutralize the amino acids before they are used for such a role; otherwise the keto-enol equilibrium would be displaced back toward the keto form by the increase in hydrogen ion concentration. The enol is necessary for bidentate coordination.

Increasing the reaction temperatures for the complexes of L-leucine, L-malic acid and D-tartaric acid with ethylenediamine had no systematic effects on the optical purity of $[\text{Co(en)}_3]^{3+}$ produced in each reaction.

In conclusion, six additional examples of asymmetric syntheses involving optically active, intermediate ligands have been demonstrated for coordination chemistry. A potential method for preparing resolved neutral complexes
such as tris-(acetylacetonato)-cobalt(III) utilizing an asymmetric synthesis has been suggested. Preliminary investigations have indicated that optically active amino acids may be used as intermediate ligands for producing such resolved complexes. Now that asymmetric syntheses have been generally exhibited for Co(III), extension of the general trend to the coordination compounds of other transition metals would be beneficial. Further work will also be necessary to determine the mechanism by which the levo rotatory amino acid complexes are formed from trans-dichloro-bis-(ethylenediamine)-cobalt(III) chloride.
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