AMINO ACID COMPLEXES OF RHODIUM(III)

APPROVED:

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AMINO ACID COMPLEXES OF RHODIUM(III)

THESIS

Presented to the Graduate Council of the North Texas State University in Partial Fulfillment of the Requirements for the Degree of

MASTER OF SCIENCE

By

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Denton, Texas
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CHAPTER I

INTRODUCTION

Of the elements of group VIII in the periodic table, complexes of cobalt(III) and platinum(IV) have been the ones most extensively studied. Rhodium compounds have not been as extensively studied as compared with compounds of cobalt. This is probably due to the cost of rhodium. (Rhodium occurs only to the extent of approximately one part per million in the earth's crust.) Also, some difficulty is experienced in obtaining rhodium in a soluble form. Rhodium complexes have been prepared in which the oxidation states of the coordinated rhodium varied from zero to plus six, inclusively.

Complexes of rhodium(III) are most abundant. An excellent reference to rhodium chemistry is Gmelins Handbuch der anorganischen Chemie. (1). In addition numerous complexes of rhodium(III) using various ligands have been reported in the literature.

Werner (2) prepared and resolved \([\text{Rh}(en)_3\text{Cl}_3]\) into its optical isomers. He noted that it was quite similar to the corresponding cobalt compound. By the use of "active racemates", Delepine (3) showed that dextrorotatory \([\text{Rh}(en)_3\text{Cl}_3]\) had the same absolute configuration as the levorotatory cobalt compound.
The catalytic racemization of optically active tris-ethylenediaminecobalt(III) iodide has long been studied. Using active carbon, platinum black, and silica gel as catalysts, Sen and Fernelius (4) have showed that the complex first is activated and then racemizes, accompanied by partial decomposition of the complex. However, the optical rotation of $[\text{Rh(en)}_3]\text{Cl}_3$ is not affected by boiling alone, or boiling with activated charcoal, platinum black, or silica gel. Optical activity remained completely unaffected by any treatment.

Dwyer and Garvan (5) have prepared pentadentate and quadradentate complexes of rhodium(III) using ethylenediaminetetraacetic acid.

Johnson and Basolo (6) have prepared and studied a number of bis-ethylenediaminerrhodium(III) complexes.

Although natural amino acid complexes of metals have been studied for many years, the only rhodium complex mentioned in the literature is $[\text{Rh}_4\text{Cl}_5(\text{H}_2\text{NCH}_2\text{CO}_2)(\text{N}_2\text{H}_3)_4\text{Cl}_2]$ (7).

In conjunction with studies on the chemical and biological properties of metal complexes of natural amino acids, several complexes of the types $[\text{Rh(en)}_2(AA)]I_2$, $[\text{Rh(AA)}_3]$, and $\text{Na}[\text{Rh(AA)}_2\text{Cl}_2]$ (en represents ethylenediamine and AA represents natural amino acid anion) were prepared and characterized.
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2. Werner, A., Berichte der Deutschen Chemischen Gesellschaft, XLV (1912), 1228-1236.


CHAPTER II

EXPERIMENTAL

Reagents

The compounds RhCl$_3$·3H$_2$O and cis- and trans-[Rh(en)$_2$Cl$_2$]NO$_3$ were prepared by the method of Anderson and Basolo (1). The amino acids used were purchased from Nutritional Biochemicals Corp., Cleveland, Ohio, and used as received.

Spectra

Infrared spectra of the amino acid complexes were run on Nujol mulls between rock-salt plates and as potassium bromide discs with a Perkin-Elmer Model 237 Grating Spectrophotometer. A Perkin-Elmer Model 21 with a calcium fluoride prism was also used in obtaining infrared spectra. Visible and near ultraviolet spectra were run on aqueous solutions with a Beckman Model DK-1 Spectrophotometer.

Optical Rotations

Measurements of optical rotations were made on aqueous solutions in a one decimeter tube at the sodium D line using a Rudolph Model 80 Precision Polarimeter.

Analytical

Carbon and hydrogen were determined by standard micro-combustion methods by C. F. Geiger, Ontario, California.
Nitrogen was determined with a Coleman Nitrogen Analyzer. Chloride was determined by adding an excess of standard silver nitrate solution to the sample and letting the mixture stand overnight protected from light. The excess silver nitrate was back-titrated potentiometrically with standard potassium chloride solution.

Preparation of (L-Aminoscid)-bis-ethylenediaminerhodium(III) iodides

A typical procedure was to slurry 3.56-g. (0.01 mole) of cis- or trans-[Rh(en)$_2$Cl$_2$]NO$_3$ and 0.01 mole of the amino acid in a mixture of 10-ml. of 1.0 M sodium hydroxide, 15-ml. of water, and 5-ml. of ethanol. The slurry was heated with occasional swirling until a clear solution resulted. The warm solution was filtered, treated with 5.0-g. solid sodium iodide, and cooled in a refrigerator overnight. The resulting cream-colored precipitate was filtered, washed with absolute ethanol, acetone, ether, and air-dried. Analytical samples were purified by recrystallization from a minimum quantity of hot water.

The results are summarized in Table I. Attempted preparation of the corresponding compounds of L-proline and L-arginine yielded a reddish-brown material of low solubility in water, containing as high as 62.3 per cent iodine.
Preparation of $\text{[Rh(glycinato)}_3]$  
A mixture of $7.41$-g. (0.1 mole) of glycine and $0.01$ mole of freshly prepared rhodium hydroxide in $50$-ml. of water was refluxed for nineteen hours. The resulting clear amber-colored solution was cooled in an ice bath. The cream-colored solid which precipitated was removed by filtration and washed with absolute ethanol, ether, and air-dried.

**Yield:** $2.36$-g. (73 per cent).

**Anal.** Calcd. for $\text{[Rh(glycinato)}_3]$: C, 22.2; H, 3.7; N, 12.9. Found: C, 21.8; H, 3.8; N, 12.8.

Preparation of $\text{[Rh(L-alaninato)}_3]$  
A mixture of $8.9$-g. (0.1 mole) of L-alanine and $0.01$ mole of freshly prepared rhodium hydroxide in $50$-ml. of water were refluxed for three days. The hot cloudy mixture was filtered and the filtrate was cooled in a refrigerator overnight. The yellowish solid which precipitated was removed by filtration and washed with absolute ethanol, acetone, ether, and air-dried.

**Yield:** $0.71$-g. (19 per cent).

**Anal.** Calcd. for $\text{[Rh(L-alaninato)}_3]$: C, 29.4; H, 4.9; N, 11.4. Found: C, 29.7; H, 5.5; N, 11.2.

Preparation of $\text{[Rh(L-leucinato)}_3]$ and $\text{[Rh(L-leucinato)}_2\text{Cl\cdot H}_2\text{O]}$

A mixture of $3.94$-g. (0.03 mole) L-leucine dissolved in $30$-ml. of $1.0 \text{ M}$ sodium hydroxide, $2.63$-g. (0.01 mole) RhCl$_3$·3H$_2$O, and $10$-ml. of ethanol were refluxed for two hours.
The hot mixture was filtered and the yellowish solid was washed with hot ethanol until the washings were colorless.

**Yield**: 0.85-g. (14.8 per cent).

**Anal. Calcd.** for \([\text{Rh}(L\text{-leucinato})_3] \cdot 4.5 \text{H}_2\text{O}\): C, 37.5; H, 7.9; N, 7.3. **Found**: C, 37.6; H, 7.3; N, 7.2.

The alcohol washings were combined and evaporated to a volume of 100-ml. on a steam bath and cooled in a refrigerator for several hours. The solid that formed was removed by filtration, washed with ether, and air-dried.

**Yield**: 0.40-g. (7.0 per cent).

**Anal. Calcd.** for \([\text{Rh}(L\text{-leucinato})_3] \cdot 4.5 \text{H}_2\text{O}\): C, 37.5; H, 7.9; N, 7.3. **Found**: C, 37.5; H, 7.1; N, 7.2.

The alcohol filtrate after removal of the above product was evaporated to dryness at room temperature under an air stream.

**Yield**: 2.74-g. (61.8 per cent).

**Anal. Calcd.** for \([\text{Rh}(L\text{-leucinato})_2\text{Cl} \cdot \text{H}_2\text{O}] \cdot 1.5 \text{H}_2\text{O}\): C, 32.5; H, 6.6; N, 6.3. **Found**: C, 32.3; H, 6.4; N, 6.0.

**Preparation of Na[\text{Rh}(L\text{-valinato})_2\text{Cl}_2] \cdot 0.5 \text{H}_2\text{O}\**

A mixture of 3.51-g. (0.03 mole) L-valine dissolved in 30-ml. of 1.0 N sodium hydroxide, 2.63-g. (0.01 mole) \(\text{RhCl}_3 \cdot 3\text{H}_2\text{O}\), and 10-ml. of ethanol was heated on a steam bath with occasional swirling for one hour. Upon cooling a gel-like mass formed in the reaction mixture. This solid was removed by filtration, air-dried for a few minutes, and washed with
ethanol and acetone which dissolved most of the solid. The ethanol and acetone washings were evaporated to dryness at room temperature under an air stream.

**Yield:** 2.34-g. (53.5 per cent)

**Anal. Calcd. for Na[Rh(L-valinato)$_2$Cl$_2$]·0.5 H$_2$O:** C, 27.4; H, 4.8; N, 6.4. **Found:** C, 27.4; H, 5.3; N, 6.5.

**Preparation of [Rh(L-phenylalaninato)$_3$] and Na[Rh(L-phenylalaninato)$_2$Cl$_2$]**

A mixture of 4.96-g. (0.03 mole) L-phenylalanine dissolved in 30-ml. of 1.0 M sodium hydroxide, 2.63-g. (0.01 mole) RhCl$_3$·3H$_2$O, and 10-ml. of ethanol was heated on a steam bath with occasional swirling for one hour. The hot mixture was filtered and the solid washed with hot ethanol, acetone, and air-dried.

**Yield:** 1.89-g. (29.2 per cent)

**Anal. Calcd. for [Rh(L-phenylalaninato)$_3$]·3H$_2$O:** C, 49.9; H, 5.6; N, 6.5. **Found:** C, 50.0; N, 6.5; H, 5.1.

The aqueous filtrate was cooled in the refrigerator and after several days a solid formed. This solid was removed by filtration, washed with ether, and air-dried.

**Yield:** 0.22-g. (3.8 per cent)

**Anal. Calcd. for Na[Rh(L-phenylalaninato)$_2$Cl$_2$]·3 H$_2$O:** C, 37.4; H, 4.5; N, 4.8. **Found:** C, 37.4; H, 4.3; N, 4.8.
Preparation of $[\text{Rh}(L\text{-tyrosinato})_3]$ and $\text{Na}[\text{Rh}(L\text{-tyrosinato})_2\text{Cl}_2]$

While heating on a steam bath, 5.43-g. (0.03 mole) of L-tyrosine was dissolved in a mixture of 30-ml. of 1.0 N sodium hydroxide, 45-ml. of water, and five extra pellets of solid sodium hydroxide. To this solution were added 2.63-g. $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and 5.0-ml. of ethanol. This mixture was heated for four hours with occasional swirling and the hot mixture was filtered. The solid residue was washed with hot ethanol. The alcohol washings were combined and evaporated to dryness. 

**Yield:** 1.41-g. (24.1 per cent).

**Anal. Calcd. for Na[\text{Rh}(L\text{-tyrosinato})_2\text{Cl}_2] \cdot 1.5 \text{H}_2\text{O}:** C, 37.0; H, 4.0; N, 4.8. Found: C, 37.1; H, 5.2; N, 4.5.

The aqueous filtrate was placed in a refrigerator and after a few days a solid appeared which was removed by filtration. The filtrate was evaporated to dryness at room temperature under an air stream and the solid was washed with ethanol. The alcohol washings were combined and evaporated to dryness. The solid from the alcohol was dried for several days in a heated vacuum dessicator at 60 degrees over magnesium perchlorate.

**Yield:** 1.44-g. (19.2 per cent).

**Anal. Calcd. for [\text{Rh}(L\text{-tyrosinato})_3] \cdot 6 \text{H}_2\text{O}:** C, 43.2; H, 5.6; N, 5.6. Found: C, 43.4; H, 4.6; N, 5.4.
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### Table I

**Preparation of \([\text{Rhen}_2(\text{AA})]_2\)**

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<tr>
<td>$[\text{Rhen}_2\text{Cl}_2]\text{NO}_3$</td>
<td>AA</td>
<td>Calcd. as</td>
</tr>
<tr>
<td>Trans</td>
<td>glycine</td>
<td>67%</td>
</tr>
<tr>
<td>Cis</td>
<td>L-alanine</td>
<td>40%</td>
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<tr>
<td>Trans</td>
<td>L-alanine</td>
<td>50%</td>
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<tr>
<td>Cis</td>
<td>L-leucine</td>
<td>37%</td>
</tr>
<tr>
<td>Trans</td>
<td>L-leucine</td>
<td>33%</td>
</tr>
<tr>
<td>Cis</td>
<td>L-methionine</td>
<td>16%</td>
</tr>
<tr>
<td>Trans</td>
<td>L-valine</td>
<td>32%</td>
</tr>
<tr>
<td>Trans</td>
<td>L-phenylalanine</td>
<td>63%</td>
</tr>
<tr>
<td>Trans</td>
<td>L-tyrosine</td>
<td>59%</td>
</tr>
</tbody>
</table>

* Calcd: I, 39.59. Found: 40.12
++ Calcd: I, 38.62. Found: 38.27

* Carbon, hydrogen and iodine analyses performed by C. F. Geiger, Ontario, California.
The (L-amino acid)-bis-ethylenediaminerhodium(III) iodides prepared by means of reaction I are summarized in

\[
\left[ \text{Rh(en)}_2\text{Cl}_2 \right] \text{NO}_3 + \text{NaAA} \rightarrow \left[ \text{Rh(en)}_2(\text{AA}) \right] \text{I}_2 \quad (I)
\]

Table I. Both the cis- and trans-\([\text{Rh(en)}_2\text{Cl}_2] \text{NO}_3\) seem to be equally well suited for the preparation of the \([\text{Rh(en)}_2(\text{AA})] \text{I}_2\) complexes. The slight differences in yields are probably not significant considering the scale of the reactions. The infrared spectra of these compounds were found to be similar to the spectra of the corresponding cobalt(III) compounds in the region 1000-4000 cm\(^{-1}\) (1).

The presence of ethanol was found to be essential for the conversion of \([\text{Rh(en)}_2\text{Cl}_2]^+\) to \([\text{Rh(en)}_2(\text{AA})]^{2+}\) in a reasonable amount of time. When ethanol was missing from the reaction mixture, no reaction was observed even after several hours of heating. These results confirm the catalytic effect of traces of ethanol on the rate of replacement of coordinated chloride ion in rhodium(III) complexes. This catalytic effect of alcohol on rhodium(III) complexes has been observed by Ouannes (2) and Delepine (3, 4). Rund and associates (5) have proposed a mechanism for this catalytic effect involving a complex of rhodium in a lower oxidation state as an intermediate.
The reddish-brown product obtained from the attempted preparation of $[\text{Rh}(en)_2(L\text{-prolinato})]I_2$ and $[\text{Rh}(en)_2(L\text{-argininato})]I_2$ was determined from infrared and visible spectra and chemical analysis to consist mainly of a mixture of cis and trans-$[\text{Rh}(en)_2I_2]I$. Experiments performed by reacting cis- or trans-$[\text{Rh}(en)_2\text{Cl}_2]\text{NO}_3$ with sodium iodide in the presence of ethanol gave a mixture of cis- and trans-$[\text{Rh}(en)_2I_2]I$ in a 90 per cent yield in both instances. The failure to prepare $[\text{Rh}(en)_2(L\text{-prolinato})]I_2$ was surprising since the corresponding cobalt(III) complex is readily made (1).

Johnson and Basolo (6) found that cis- or trans-$[\text{Rh}(en)_2\text{Cl}_2]\text{NO}_3$ appeared to react with retention of geometric configuration when the coordinated chloride was replaced with other anions. Since all the complexes of the type $[\text{Rh}(en)_2(\text{AA})]I_2$ reported here must have the cis- configuration, it seems obvious that a rearrangement occurs readily when trans-$[\text{Rh}(en)_2\text{Cl}_2]\text{NO}_3$ is heated in the presence of ethanol and an amino acid. The presence of a labile complex of rhodium in a lower oxidation state, formed by reduction with ethanol, would explain the ready isomerization.

The (L-amino acid)-bis-ethylenediaminerhodium(III) complexes are quite stable and are easily recrystallized from water. Since all the products show low optical rotations, it appears that the two possible diastereoisomers are produced in approximately equal amounts. No indication of appreciable
solubility differences of the diastereoisomers was found. This is different from previous experiences with similar complexes of cobalt(III) (1).

Several attempts were made to replace the coordinated amino acid in the complex \([\text{Rh(en)}_2(\text{L-phenylalaninato})]_2\). This complex was chosen because of the high yield and high molecular weight of this complex.

Sodium cyanide had no appreciable effect on a solution of this complex. Aqueous ethylenediamine (25% per cent) also showed only a minor effect. Likewise, potassium iodide solution after heating for several hours in the presence of alcohol affected the complex only to a small extent. In each of the above instances infrared spectra and chemical analysis of the products indicated that while apparently some change took place, it occurred only to a small extent.

Spectra of aqueous solutions of \([\text{Rh(en)}_2(\text{L-phenylalaninato})]_2\) showed a single absorption band from 260–280 μμ. The spectra of solutions of this complex in 0.4 M hydrochloric acid and 0.4 M sodium hydroxide were identical with the neutral solution, even after boiling for one hour.

The antimonyl-\(\delta\)-tartrate of \([\text{Rh(en)}_2(\text{L-phenylalaninato})]^2+\) was easily made by reaction of the iodide of the complex with silver antimonyl-\(\delta\)-tartrate. Recrystallization of the resulting salt from water resulted in a clear tar; however, the salt could be crystallized from mixtures of ethanol and water.
Fractional crystallization of the antimonyl-α-tartrate resulted in two fractions. The more soluble fraction had a molecular rotation of +752°; the lesser soluble fraction had a molecular rotation of +900°. The fractions were reconverted to the iodide by removal of the antimonyl-α-tartrate with silver nitrate, then precipitating the iodide with an excess amount of sodium iodide. The iodide from the more soluble fraction had a molecular rotation of -166°. The iodide from the less soluble fraction had a molecular rotation of -91°. It is highly unlikely that this represents complete resolution.

Attempts to prepare the tris-(L-amino acid)rhodium(III) complexes using stoichiometric quantities of amino acid and rhodium chloride (reaction II) resulted in some cases in complexes of the types Na[Rh(AA)_2Cl_2] and [Rh(AA)_2Cl_H_2O]. These structures were assigned on the basis of chemical analyses. The visible and near ultraviolet spectra of these complexes were all quite similar, having a single absorption band at approximately 285-450 mp. In general these complexes were hygroscopic and ranged in color from almost colorless to brown, many of the complexes having a pale yellow color.

The isolation of complexes having only two coordinated amino acid ligands instead of three from the reactions between rhodium chloride and sodium salts of the amino acids in the
presence of ethanol seems to indicate that some sort of equilibrium controls the formation of the tria-amiino acido complexes.

Another method for preparing tria-amiino acido complexes is a reaction between rhodium hydroxide and free amino acid (reaction III). This method was used successfully in preparing [Rh(glycinato)₃] and [Rh(L-alaninato)₃], however, when a mixture of L-leucine, rhodium hydroxide, and water was refluxed no noticeable reaction occurred after five days. When L-proline was used, a large amount of rhodium metal precipitated. The success or failure of this method may depend either upon the acid strength or the solubility of the amino acid used or both. For example glycine and L-alanine are soluble in water while L-leucine has a relatively low solubility. Also the water solubility of the complex probably has some effect.
1. Hu, James and Burl E. Bryant, unpublished notes, Department of Chemistry, North Texas State University, Denton, Texas, 1964.


APPENDIX

The infrared spectra of the compounds prepared and discussed are reproduced on the following pages.
Fig. 1--Infrared Spectra of \( \text{cis-}[\text{Rh(en)}_2\text{Cl}_2] \text{NO}_3 \).
Fig. 2—Infrared Spectra of trans-[Rh(en)₂Cl₂]NO₃.
Fig. 4--Infrared Spectra of $[\text{Rh(en)}_2(\text{L-alaninato})] \text{I}_2$. 
Fig. 6--Infrared Spectra of [Rh$(en)_2$(L-leucinato)]$I_2$. 
Fig. 7--Infrared Spectra of $[\text{Rh(en)}_2(\text{L-valinato})] \text{I}_2$. 
Fig. 10--Infrared Spectra of $\text{[Rh(glycinato)}_3]$. 
Fig. 12—Infrared Spectra of \([\text{Rh}(\text{L-leucinato})_3]\cdot 4.5 \text{H}_2\text{O}\).
Fig. 14—Infrared Spectra of $\text{[Rh(L-valinato)$_2$Cl$_2$]} \cdot 0.5 \text{H}_2\text{O}$. 
Fig. 18--Infrared Spectra of $\left[\text{Rh}(L\text{-tyrosinato})_2\text{Cl}_2\right] \cdot 1.5 \text{ H}_2\text{O}$.
Fig. 20--Infrared Spectra of $[^{Rh(en)}_2I_2]$ I prepared from trans-$[^{Rh(en)}_2Cl_2]$ NO$_3$. 

(Mafol mull)
Fig. 21—Infrared Spectra of $\left[\text{Rh}(\text{en})_2\text{I}_2\right]$ I prepared from $\text{cis-}\left[\text{Rh}(\text{en})_2\text{Cl}_2\right] \text{NO}_3$. 

(Mujol mull)
Fig. 22--Infrared Spectra of the product from the reaction of $[\text{Rh(en)}_2(\text{L-phenylalaninato})]$ $I_2$ with aqueous ethylenediamine.
Fig. 22 (continued).
Fig. 23--Infrared Spectra of the product from the reaction of \([\text{Rh(en)}_2(\text{L-phenylalaninato})]I_2\) with Na CN.
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