

TRANSITION-METAL COMPLEXES WITH
OPTICALLY ACTIVE LIGANDS

A Thesis
submitted for the
Degree of Doctor of Philosophy
of the University of London
by

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July 1965

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- 2 -

To my mother and father.

ACKNOWLEDGEMENTS

I should like to thank my supervisor, Professor G. Wilkinson, F.R.S., for his advice and encouragement. I am extremely grateful to Dr. R.D. Gillard, who guided me in this work, for his help and inspiration. I am also indebted to many of the staff and research students of the Chemistry Departments of Imperial College and Sheffield University for their help at various times. I thank Mrs. D.M. McCleverty for typing the manuscript.

ABSTRACT

Transition-metal complexes with optically active ligands have been studied to elucidate the absolute configurations of dissymmetric complexes, to correlate the configurations of asymmetric ligands, to study the origin of the optical activity of these complexes and their electronic spectra and finally to examine the equilibria between diastereoisomers. A conformational theory of stereospecificity has been used to assign the absolute configurations of the $(-)[Cr(-pn)_3]^{3+}$ and the $(+)[Rh(-pn)_3]^{3+}$ ions. The circular dichroisms of these complexes were used to assign the absolute configurations of the corresponding ethylenediamine complexes. The absolute configuration of $(+)$ trans-cyclopentane-1,2-diamine has been ⁿdetermined for the first time and the Cotton effects of many metal complexes, principally cobalt(III) complexes with asymmetric diamines were used to confirm the absolute configurations of the four other diamines. The equilibria between the diastereoisomers in the $Co(amino-acidate)_3$ and $Co(+formylcamphor)_3$ systems were studied. With L-alanine as the amino-acid no stereospecificity was observed but with L-glutamic acid there was a considerable difference in free energy between the diastereoisomers. Marked stereospecificity was also observed in the diketonato complex. The effect of the solvent on the optical activity of $(-)Co(+formylcamphor)$ was shown to be dipolar in nature.

The acidotetramminecobalt(III) and the acidopentamminecobalt(III) complexes with α -amino-acids and α -hydroxy-acids have been prepared. The Cotton effects of these complexes allowed the relative configurations of the two classes of acids to be compared for the first time by a physical method. The Cotton effects, which are associated with the metal atom in these complexes, provided the first unambiguous evidence of a vicinal effect in co-ordination compounds. This vicinal effect has been used in tetragonal complexes of cobalt(III), rhodium(III) and nickel(II) to identify magnetic-dipole allowed transitions, which could not have been identified easily in any other way. Finally an electronic spectral investigation of the copper(II) tartrate complexes with active and racemic tartaric acids has showed that the differences, which had previously been observed between these two compounds, can only be explained by the presence of polynuclear complexes.

	Page
Abstract	4
<u>Chapter I Introduction</u>	8
Selection Rules	11
Optical Activity	18
Absolute Configuration	21
Stereospecificity	25
<u>Chapter II The Absolute Configuration of Diamines and of their Complexes with Trivalent Metals</u>	31
<u>Chapter III Trisamino-acidate and Trisformylcamphor Complexes of Cobalt(III) and Rhodium(III)</u>	
Metal(amino-acidate) ₃ Complexes	47
Metal(+formylcamphor) ₃ Complexes	76
A Solvent Effect of (-)Tris(+)formylcamphorcobalt(III)	85
<u>Chapter IV The Vicinal Effect</u>	
Acidopentammine and Acidotetramminecobalt(III) Complexes	90
Tetragonal Cobalt(III) and Rhodium(III) Complexes	103
Tetragonal Nickel(II) Complexes	109

	Page
<u>Chapter V</u> <u>Stereospecificity in Copper(II)</u>	115
<u>Tartrate Complexes</u>	
<u>Experimental Section</u>	135
References	165

CHAPTER I

INTRODUCTION

Werner introduced the technique of optical resolution into inorganic chemistry. With this powerful tool he demonstrated the three-dimensional structure of many transition-metal complexes and thus started the investigation into the structure of these complexes. The method of comparing the relative configurations of resolvable metal complexes did not follow the degradative methods⁽¹⁾, which were used to elucidate the configurations of organic compounds. The mechanisms of the reactions of organic compounds are sufficiently understood to allow the relative configurations of two organic compounds to be deduced from the conversion of one into the other. If an organic compound can be degraded to (+)glyceraldehyde, then its configuration relative to that compound can be given. The later development of the study of the reaction mechanisms of metal complexes has caused the chemical correlation⁽²⁾ of these complexes to be overshadowed by the more reliable physical methods. The assignment of the relative configurations of inorganic compounds has therefore developed in a different way.

The physical effects, which have been used by inorganic chemists to study the configurations of resolvable complexes, are manifestations of the general effect named after Cotton.

The Cotton effect⁽³⁾ is observed in the neighbourhood of an electronic absorption band and is detected in three ways:

- 1) The anomalous dispersion of the optical rotation - commonly known as optical rotatory dispersion, which will be abbreviated O.R.D.
- 2) The differential absorption of right and left circularly polarised light - commonly known as circular dichroism.
- 3) The ellipticity of the light used to measure the rotation.

The relationship between the optical rotatory dispersion, the circular dichroism and the electronic absorption spectrum is shown in Figure 1. The Cotton effect is said to be positive

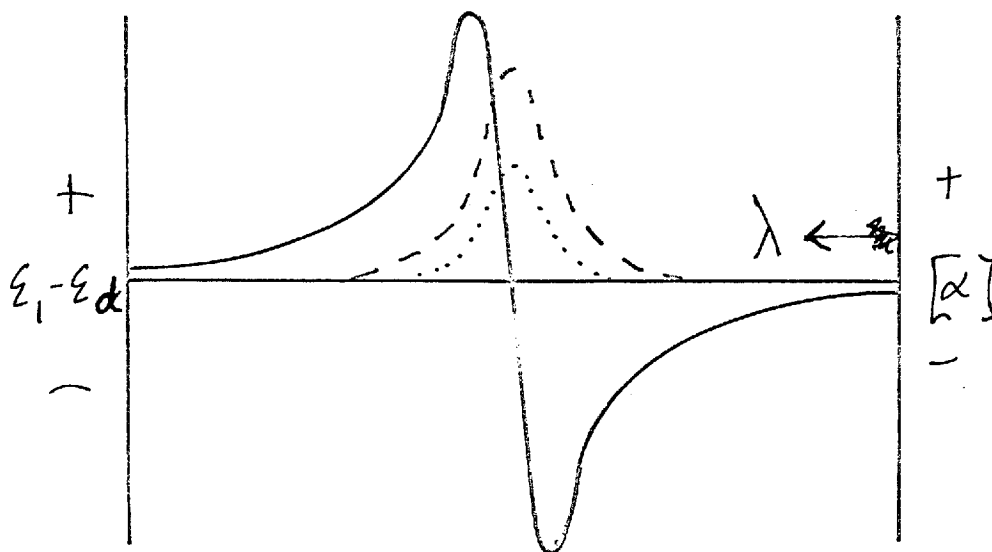


Figure I. The Cotton Effect.

- _____ O.R.D. curve.
- Circular dichroism ($\Sigma_l - \Sigma_d$).
- Electronic absorption band.

if the circular dichroism is positive or if the O.R.D. peak at longer wavelength is positive. The electronic absorption bands of most transition metals are in the visible region of the spectrum. The Cotton effects, which are associated with these absorption bands, therefore occur in a region where they are easily detected and measured. It is probably this factor which has led to the greater use of the Cotton effect by inorganic chemists than by organic chemists.

The assignment⁽⁴⁾ of the configuration of a resolvable compound by the sign of the optical rotation at a certain wavelength is of no value. Later attempts⁽⁵⁾ to assign the configuration by the sign of the long-wavelength Cotton effect were also unsatisfactory, because the origin of the effect was still largely unknown. However, before the second World War the O.R.D. and the circular dichroisms of a large number of metal complexes were obtained. The principal workers were F.M. Jaeger, W. Kuhn, I. Lifschitz, J.P. Mathieu and P. Pfeiffer. The great advances in the understanding of the electronic absorption spectra of transition-metal complexes since the last war has led to the reinvestigation of much of the older work. The relationship between the Cotton effects and the electronic absorption spectrum is now known. The assignment of the configuration of a metal complex now has a reliable

theoretical foundation. An understanding of the origin of the electronic absorption spectra of transition metal complexes is essential before their configurations can be assigned.

Selection Rules

Transition metals have partly filled d shells. Electrons in partly filled shells interact with one another. In the metal complexes, which have been studied in this thesis, the interaction is of the Russell-Saunders⁽⁶⁾ type. This interaction produces further energy levels. The Russell-Saunders theory however deals only with free ions. In a chemical environment these levels are further split according to the symmetry of the chemical environment. The original theory of Bethe⁽⁷⁾, which describes this splitting, was purely electrostatic. Other theories which consider covalent bonding use the same symmetry arguments.

The transitions between these energy levels are not equally allowed. Selection rules, obtained from experimental observations, describe the allowedness of the electronic transitions. A measure of the allowedness of a transition is the size of the oscillator strength of that transition. The oscillator strength is determined experimentally by measuring the area under the absorption curve. Mulliken⁽⁸⁾ has related the oscillator strength to the dipole strength of the transition.

The dipole strength of the transition between the states ψ_1 and ψ_2 is given by the equation:

$$\sqrt{D} = Q = \int \psi_1 M \psi_2 d\tau$$

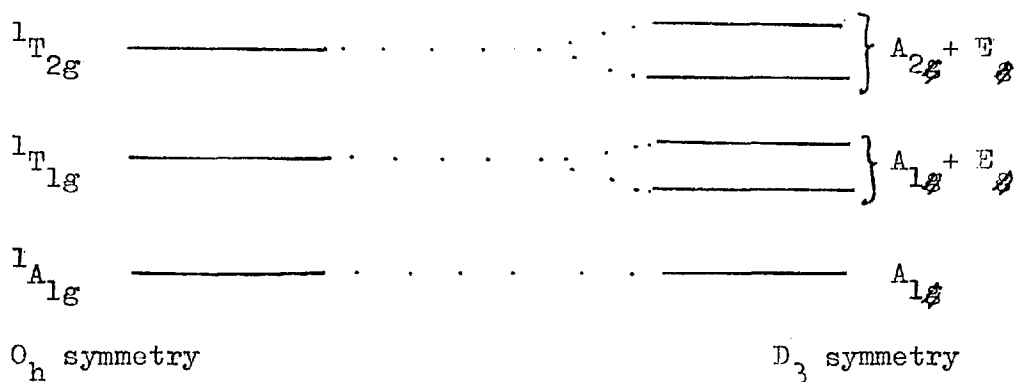
where Q is the transition moment and M is the dipole moment vector. The transition moment is a physical property of the molecule and therefore must be invariant under the symmetry operations of the molecule. The intensity of the absorption depends on the size of the integral. The conditions, under which the integral has a non-zero value for the various possible pairs of states, are known as selection rules. An electronic transition is only allowed if the direct product of the integral contains the A_{1g} representation. The dipole moment vector represents the charge displacement during the transition. There are two types of dipole moment:

- 1) An electric-dipole moment. This is produced by the translation of electric charge. The vector has therefore the symmetry properties of a translation. Translations belong to ungerade representations.
- 2) A magnetic-dipole moment. This is produced by the rotation of electric charge. The vector has therefore the symmetry properties of a rotation. Rotations belong to gerade representations.

There are two mechanisms for the absorption of radiation.

The more common is the electric-dipole mechanism. In d-d transitions, the direct product of the electric-dipole transition moment integral cannot contain the A_{1g} representation because the electric-dipole vector is ungerade while the states involved in the electronic transitions are both gerade. The intensities of d-d transitions, which are observed arise from vibronic coupling and are about 10^{-3} of the value for electric-dipole allowed transitions. The magnetic-dipole mechanism⁽⁹⁾ is less common. Electronic transitions between two gerade states or between two ungerade states will be magnetic-dipole allowed. Therefore d-d transitions can be magnetic dipole allowed. Group theory cannot give a quantitative value to the transition moment, but it can show if the particular transition is electric or magnetic-dipole allowed.

The application of group theory to the determination of the selection rules is best shown by an example. The compound chosen for this is trisethylenediaminecobalt(III) chloride. The visible spectrum of this compound is very similar to that of hexamminecobalt(III) chloride. It is therefore obvious that the symmetry of the chromophoric group is approximately O_h . The electronic transitions of the spin-paired configuration in O_h and D_3 symmetry are given in Diagram I.



There are two absorption bands in the visible spectrum of these compounds. In the O_h group the electric dipole forms a basis for the T_{1u} representation. The direct product representations of the transition moment integrals are given in Table 1.

Table 1

Transition	Integral	Direct Product
${}^1T_{2g} \leftarrow {}^1A_{1g}$	${}^1T_{2g} \times T_{1u} \times {}^1A_{1g}$	$A_{1u} + E_u + T_{1u} + T_{2u}$
${}^1T_{1g} \leftarrow {}^1A_{1g}$	${}^1T_{1g} \times T_{1u} \times {}^1A_{1g}$	$A_{2u} + E_u + T_{1u} + T_{2u}$

The transitions are therefore electric-dipole forbidden and require vibronic coupling to provide the intensity that is experimentally observed.

The Cotton effect is intimately connected with magnetic-

dipole allowed transitions. Therefore when the magnetic-dipole allowedness of the electronic transitions of trisethylenediamine-cobalt(III) chloride is being considered the cation is treated as if it belonged to the resolvable D_3 group. The decrease in symmetry splits the ${}^1T_{1g}$ and the ${}^1T_{2g}$ levels as shown in the diagram above. In the D_3 group the magnetic-dipole vector forms a basis for the A_{2g} and the E_g representations. The allowedness of the transitions can be deduced from Table 2.

Table 2

Selection rules for magnetic-dipole
transitions in D_3 symmetry

Transition	Direct Product of Integral		Polarisation
	z axis	xy axis	
${}^1A_{2g} \leftarrow {}^1A_{1g}$	A_{1g}	E_g	z ()
${}^1E_g \leftarrow {}^1A_{1g}$	E_g	$A_{1g} + A_{2g} + E_g$	xy ($\perp$)
${}^1A_{1g} \leftarrow {}^1A_{1g}$	A_{2g}	E_g	forbidden
${}^1E_g \leftarrow {}^1A_{1g}$	E_g	$A_{1g} + A_{2g} + E_g$	xy ($\perp$)

The magnetic-dipole transition moment vector representation in the z axis is A_{2g} and in the xy axis is E_g .

There should be no g subscripts in this Table.

The selection rules for magnetic-dipole transitions for spin-free d^3 and spin-paired d^6 electron configurations in several different point groups are given in Table 3. The table describes how the T_{1g} and the T_{2g} levels are split as the symmetry is lowered. The representations of the rotations in the three axes are given for each point group. From these the allowedness of the transitions can be obtained.

An examination of the circular dichroisms of the cobalt(III) complexes, that have been published, shows that the rotational strength of magnetic-dipole allowed band II transitions is very much smaller than the allowed band I transitions. This suggests that the rotational strengths of the transitions are very much controlled by the selection rules for O_h symmetry. It also appears that the selection rules of a complex seem to be governed by the symmetry of the principal rotation axis of that complex.

Table 3

Selection rules for magnetic-dipole allowed transitions for
 d^3 and d^6 electronic configurations

Symmetry of Chromophore		O_h	D_3	C_3	D_{4h} and C_{4v}	C_{2v}	C_s	C_1
Representation of magnetic-dipole moment vector	R_z	T_{1g}	A_2	A	A_2	A_2	A^{11}	A
	R_x	T_{1g}	E	E	E	B_1	A^{11}	A
	R_y	T_{1g}	E	E	E	B_2	A^{11}	A
d^6 spin-paired ground state	ground state	A_{1g}	A_1	A	A_1	A_1	A^1	A
(singlets)	excited states	$T_1 ()(\perp)$	$A_2 () E(\perp)$	$A () E(\perp)$	$A_2 () E(\perp)$	$A_2 () 2B(\perp)$	$A^1 () 2A^{11}(\perp)$	3A
		$T_2 (-)$	$A_1 (-) E(\perp)$	$A () E(\perp)$	$B_2 (-) E(\perp)$	$A_1 (-) 2B(\perp)$	$2A^1 () A^{11}(\perp)$	3A
d^3 spin-free ground state	ground state	A_{2g}	A_2	A	B_1	A_2	A^{11}	A
(quartets)	excited states	$T_{2g} ()(\perp)$	$A_1 () E(\perp)$	$A () E(\perp)$	$B_2 () E(\perp)$	$A_1 () 2B(\perp)$	$2A^1 () A^{11}(\perp)$	3A
		$T_{1g} (-)$	$A_2 (-) E(\perp)$	$A () E(\perp)$	$A_2 (-) E(\perp)$	$A_2 (-) 2B(\perp)$	$A^1 () 2A^1(\perp)$	3A

(||), polarisation along z axis. ($\perp$), polarisation along x and y axes. (-), forbidden transition.

All transitions are allowed in the C_1 point group

Selection rules for C_2 are as for C_s but the components are A and B.

Optical Activity

When an electron moves along a helical path, the translatory motion produces an electric-dipole moment and the rotatory motion produces a magnetic-dipole moment. These two moments are parallel or anti-parallel according to the right or left-handedness of the helical motion. From this physical model Drude⁽¹⁰⁾ showed that the optical rotation at a particular wavelength could be considered as the sum of the contributions from a number of absorption bands. However his expression was not valid in the regions where there was anomalous dispersion of the optical rotation. Rosenfeld⁽¹¹⁾ applied the quantum theory to this helical model and derived an expression for the rotation, which was very similar to Drude's.

$$\phi = \frac{K \sum R_{12} \nu_{12}}{\nu_{12}^2 - \nu^2}$$

ϕ is the rotation at a frequency ν . ν_{12} is the frequency of the transition from the state ψ_1 to the state ψ_2 . R_{12} is the rotatory power of this transition. It can be obtained from the equation:-

$$R_{12} = pU \cos \theta$$

where p and U are the real electric and magnetic transition moments. θ is the angle between these moments. The condition for optical rotation to be observed in a compound is that R_{12}

must have a finite value. This condition is fulfilled when a transition is simultaneously magnetic and electric-dipole allowed. Only molecules, which belong to point groups, in which translations along an axis and rotations about that axis, have representations in common, can have electronic transitions, which will give rise to optical rotatory power. An examination of the symmetry elements of such groups shows that the following elements of symmetry are not present: a centre of inversion, a plane of symmetry and an alternating rotation-reflection axis. This is the theoretical justification of Pasteur's⁽¹²⁾ statement that the molecule should be non-superposable on its mirror image to be optically active. Drude⁽¹⁰⁾ showed that a right-handed helix absorbed left circularly polarised light more than right circularly polarised light. The circular dichroism, which is defined as $\epsilon_l - \epsilon_d$, and the optical rotation are therefore positive, when an electron moves in a right-handed helix. This is confirmed by the circular dichroism⁽¹³⁾ of (+)trisethylenediaminecobalt(III) chloride in the solid state.

It is obvious that if an electronic transition must be magnetic-dipole allowed to produce a Cotton effect associated with the transition, then circular dichroism can be used to identify magnetic-dipole allowed transitions. Mason⁽¹⁴⁾ has used the size of the Kuhn dissymmetry factor⁽¹⁵⁾ g as a criterion

for magnetic-dipole allowed transitions. The oscillator strengths of magnetic-dipole allowed transitions are about 10^{-2} times smaller than the oscillator strengths of electric-dipole allowed transitions. Magnetic-dipole allowed transitions are rather difficult to detect by other methods⁽¹⁶⁾.

A recent review⁽¹⁷⁾ describes the many theories of optical activity. Unfortunately the theories of the optical activity of transition-metal complexes have concentrated on the optical activity of trisdiamine or trisoxalatometal complexes. In such complexes the metal atom is at an asymmetric centre. The optical activity of metal complexes, in which the metal atom is not asymmetrically co-ordinated but is co-ordinated to an optically active ligand, has hardly been studied at all. The vicinal effect - that is the effect of one atom or group in a molecule on a neighbouring atom or group in the same molecule, has not been considered in these theories of optical activity. The vicinal effect is recognised in the theories, which deal with the optical activity of organic molecules. The failure to recognise the vicinal effect in the optical activity of metal complexes has led to considerable confusion in the past. A whole chapter in this thesis is therefore devoted to the study of the optical activity in tetragonal complexes and in complexes with no chelate rings.

Absolute Configuration

The determination⁽¹⁸⁾ of the absolute configuration of sodium rubidium(+)tartrate by a crystallographic method is the most important contribution to the study of configurations. Previously the assignment of optical configurations had been purely relative to an arbitrarily chosen standard configuration⁽¹⁹⁾. After the crystallographic determination, configurations could be related to a compound, whose absolute configuration was known. The same crystallographic method was used to determine the absolute configuration of (+)trisethylenediaminecobalt(III)⁽²⁰⁾ chloride and three other cobalt(III) complexes⁽²¹⁾⁽²²⁾⁽²³⁾. The other important contribution was the explanation of the origin of the Cotton effects of transition-metal complexes by Moffitt⁽²⁴⁾. The Cotton effects of transition-metal complexes could now be reliably used to compare the configurations of the complexes with the known absolute configuration of (+)[Coen₃]Cl₃. It has been found that the circular dichroisms of metal complexes are easier to interpret than the O.R.D. curves of these complexes. The overlap of several Cotton effects complicates the O.R.D. more than the circular dichroism. Circular dichroism is therefore the preferred technique for the comparison of configurations. Before a comparison can be made, the electronic transitions, which produce the observed Cotton effects must be identified. Polarised absorption spectra and polarised circular

dichroism measurements⁽²⁵⁾ in the solid state have been an invaluable tool for this.

Mason⁽¹³⁾ measured the circular dichroism of $(+)[\text{Coen}_3]\text{Cl}_3$ in the solid state and in solution. The crystallographic study⁽²⁰⁾ had shown that the absolute configuration of this complex was as is shown in Figure 2. It also showed that the C_3 axis of the

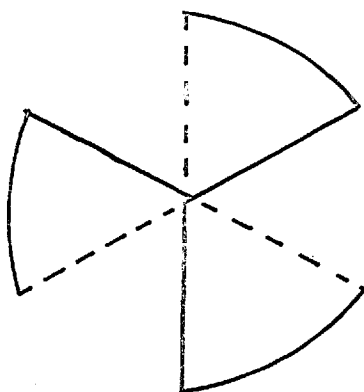
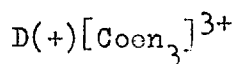


Figure 2.



This is a left-handed helix.

complex was parallel to the optic axis of the crystal. Mason directed the circularly polarised light along the optic axis. Therefore only the transition which is perpendicular to the C_3 axis produced a Cotton effect. This ${}^1\text{E}_g \leftarrow {}^1\text{A}_{1g}$ transition had a positive rotational strength. Mason therefore suggested that dihedral spin-free d^3 and spin-paired d^6 complexes have

the same absolute configuration as the $(+)[\text{Coen}_3]^{3+}$ ion if the spin-allowed transition of lowest energy has an E component with a positive rotatory power. If this transition in the metal complex can be identified then the absolute configuration of the complex can be given. Mason⁽²⁶⁾ studied the Cotton effect of a charge transfer absorption in a $(-)$ tris(1:10-phenanthroline)-ruthenium(II) complex. The electronic transition of this absorption band was directed along the C_3 axis of the complex. The Cotton effect had a negative rotational strength; therefore right circularly polarised light had been preferentially absorbed by this electronic transition. The C_3 axis of this complex is therefore a left-handed helix and has the same chirality as the $(+)[\text{Coen}_3]^{3+}$ ion. Unfortunately the charge transfer bands of this complex obscured the d-d transitions so it has been impossible to use this method as a check on the previous comparative method. Another spectroscopic method⁽²⁷⁾ has used the variation of the circular dichroisms of metal complexes, which is caused by ion-pair formation as a method of comparing configurations.

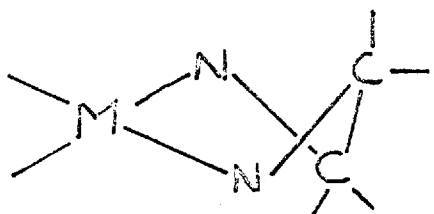
The spectroscopic methods of comparing the configurations of transition-metal complexes have replaced the methods⁽²⁸⁾ based on the solubility of the diastereoisomers. This method was early criticised⁽²⁹⁾. However it has been used considerably⁽³⁰⁾.

The method is, in the majority of compounds, consistent with the optical methods but there are anomalies. A similar but less empirical method is the method of active racemates⁽³¹⁾. A biological method⁽³²⁾ has been reported. These empirical methods should always be used with caution.

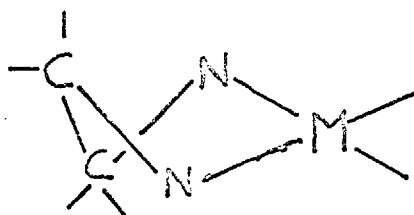
There are several conventions, which have been used to describe the absolute configuration of a metal complex. At first the symbols D and L were borrowed from organic chemistry. Piper⁽³³⁾ suggested that these symbols be replaced by Λ and Δ to emphasise that the configurations were not being compared with organic compounds. Gillard⁽³⁴⁾ has suggested that the helicity of the rotation axes of the complex is the most rigorous definition of the absolute configuration. In this convention the $(+)[\text{Coen}_3]^{3+}$ ion would be described as $S(C_3)R(C_2)$ - that is the C_3 axis is a left-handed helix while the C_2 axis is a right-handed helix. Mason⁽²⁵⁾ has produced a variation of this convention. Hawkins and Larsen⁽³⁵⁾ have applied the octant rule⁽³⁶⁾ to transition-metal complexes. However this method is only useful for complexes, in which the metal is not asymmetrically co-ordinated.

Stereospecificity

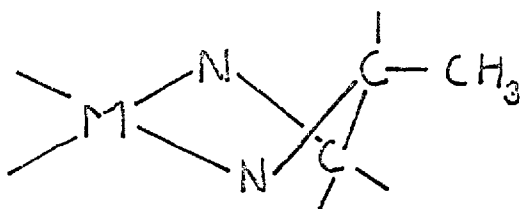
The phenomenon of stereospecificity in transition-metal complexes has been reviewed several times⁽³⁷⁾⁽³⁸⁾⁽³⁹⁾⁽⁴⁰⁾. Corey and Bailar⁽³⁸⁾ introduced conformational analysis to the study of stereospecificity in diamine complexes. The chelate ring formed by a transition-metal and a diamine has been shown⁽⁴¹⁾ to be puckered. Corey and Bailar demonstrated that this puckered ring could exist in two conformations, designated K and K', which are enantiomeric. These are illustrated in Figure 3. In an isolated ethylenediamine chelate ring the two conformations will have the same energy. However, when two or three ethylenediamine molecules are co-ordinated to the same metal atom, steric interactions occur between the chelate rings. If one configuration of $[\text{Coen}_3]^{3+}$ is considered, say the $S(C_3)R(C_2)$ configuration, then the chelate rings can have the following combinations of the two conformations: KKK, KKK' and K'K'K'. Corey and Bailar examined the steric repulsions in these isomers and showed that the KKK isomer was the most stable. The difference in stability between this isomer and the least stable isomer, the K'K'K' isomer, is 1.8 kcals per mole. The KKK isomer is called the "lel" isomer as the C-C bonds in the chelate ring are parallel to the C_3 axis, while the K'K'K' isomer is referred to as the "ob" isomer because in that conformation the C-C bonds are oblique



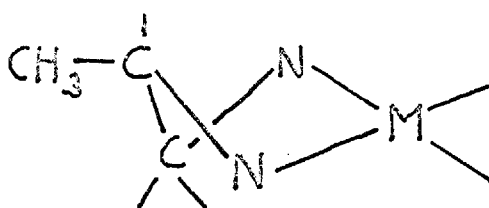
K ring



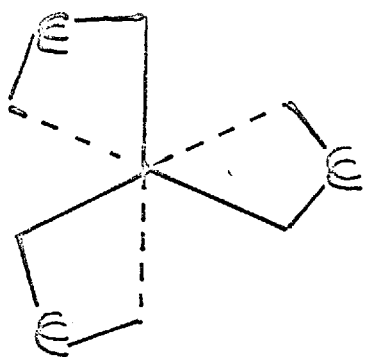
K' ring



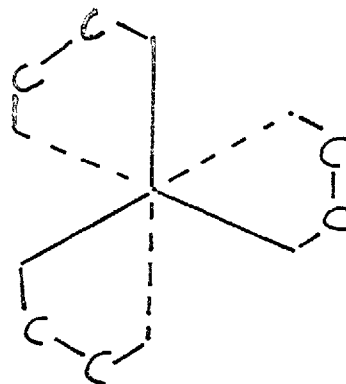
K ring with
(+)propylenediamine



K' ring with
(-)propylenediamine



three K rings
"lel" isomer



three K' rings
"ob" isomer

Figure 3.

to the C_3 axis. If the $R(C_3)S(C_2)$ configuration of $[Coen_3]^{3+}$ is chosen, then the $K'K'K'$ isomer is the "lel" isomer and is the more stable form. This must be so because the (+) and the (-) isomers of $[Coen_3]^{3+}$ are enantiomorphous. The more stable isomer is always the "lel" isomer, but it can be either KKK or $K'K'K'$ depending on the absolute configuration of the metal atom. The "lel" and "ob" forms are shown in Figure 3. If an asymmetric diamine, such as propylenediamine is used instead of ethylenediamine, then the methyl substituent in the diamine ring can occupy either an axial or an equatorial position. The equatorial position is favoured. Therefore the absolute configuration of the diamine will determine the configuration of the most stable isomer. This is shown in Figure 3, where (+)propylenediamine assumes the K' conformation, while the (-)diamine assumes the K conformation. Using this argument Corey and Bailar showed that the most stable isomer of $[Co(+pn)_3]^{3+}$ will have the D or the $S(C_3)R(C_2)$ configuration, while the most stable isomer of $[Co(-pn)_3]^{3+}$ has the $LCo(K'K'K')$ configuration, which has the same thermodynamic stability as the $DCo(KKK)$ configuration. Corey and Bailar's assignment of the absolute configuration of the $(+)Co(+pn)_3]^{3+}$ ion has been confirmed by a crystallographic determination⁽²²⁾. The O.R.D. curves⁽⁴²⁾ of $(+) [Co(+pn)_3]^{3+}$ and the $(+) [Coen_3]^{3+}$ ions are

identical, which is also a confirmation of Corey and Bailar's theory. In chapter II of this thesis this theory is used to predict the absolute configurations of asymmetric diamines and of metal(diamine)₃³⁺ ions.

One of the principal conclusions that Corey and Bailar obtained from their study of diamine complexes was that the less stable isomers should be present at equilibrium in detectable amounts. Dwyer and his co-workers⁽⁴³⁾ have found these less stable isomers and have shown that they are present in the amounts predicted by the theory. However there has been very little quantitative work done on metal complexes with bidentate ligands other than diamines. Lifschitz⁽⁴⁴⁾⁽⁴⁵⁾⁽⁴⁶⁾⁽⁴⁷⁾ was able to isolate several isomers of Co(amino-acidate)₃ complexes. This was taken by some⁽³⁷⁾⁽⁴⁸⁾ as evidence of the stability of the chelate rings. Others^(43a) assumed that the detection of several isomers was evidence of the small difference in free energy between the isomers. Two reports⁽⁴⁹⁾ have stated that there is no stereospecificity in [Coen₂(amino-acidate)]²⁺ ions. However there is good evidence⁽⁵⁰⁾ for complete stereospecificity in Co(+formylcamphor)₃ and Cr(+formylcamphor)₃ complexes. The qualitative studies however have been done on more labile complexes. Stereospecificity has been found in bishistidinatocobalt(II)⁽⁵¹⁾ bisasparaginatocopper(II)⁽⁵²⁾ and nickel(II) complexes with Schiff bases⁽⁵³⁾. No stereospecificity

has been detected in bisalaninatocopper(II)⁽⁵⁴⁾ but Fromaeus⁽⁵⁵⁾ has shown that active and racemic copper(II) tartrates have different stabilities.

Crystallographic results indicate that the chelate ring of β -diketones⁽⁵⁶⁾ is planar and that the chelate ring of α -amino-acids⁽⁵⁷⁾ is only slightly puckered. The theory of Corey and Bailer cannot be used to explain the stereospecificity in these compounds. It is interesting that stereospecificity was detected with ligands, which were all polydentate. The $\text{Co}(\text{amino-acidato})_3$ and the $\text{Co}(+\text{formylcamphor})_3$ complexes have been reinvestigated with modern techniques to try to isolate all the possible isomers and to see if an equilibrium exists between them. By determining the relative amounts of the isomers, the quantitative results are obtained on which a stereospecific theory can be based. This is just the application of Dwyer's⁽⁴³⁾ work on diamine complexes to amino-acid and β -diketone complexes.

A whole chapter of the thesis is devoted to an explanation of the many observations made on the stereospecificity in copper(II) tartrates. This is a very complex system and the investigation has been qualitative. The crystal structures of none of these complexes has been determined. We can only predict very roughly what stereospecificity if any will be observed. The purpose of this work is to obtain quantitative results and to use these data

to explain previous observations and if possible to help with the assignment of the absolute configuration of transition-metal complexes.

CHAPTER II

THE ABSOLUTE CONFIGURATIONS OF DIAMINES AND OF THEIR COMPLEXES WITH TRIVALENT METALS

In chapter I the older methods of comparing the configurations of metal complexes were discussed and were shown to be unreliable. The crystallographic determination⁽²⁰⁾ of the absolute configuration of the $(+)[\text{Coen}_3]^{3+}$ ion combined with Mason's⁽¹³⁾ measurement of the circular dichroism of this ion in the solid state provided the essential knowledge for the correct assignment of the absolute configuration of $[\text{Co}(\text{diamine})_3]^{3+}$ ions and the analogous chromium(III) and rhodium(III) ions. The configuration of a trisdiamine complex of a metal, which has a visible spectrum analogous to that of the $[\text{Coen}_3]^{3+}$ ion, can be compared by its O.R.D. curve or by its circular dichroism with the known absolute configuration of the $(+)[\text{Coen}_3]^{3+}$ ion. Corey and Bailer's⁽³⁸⁾ use of conformational analysis to determine the absolute configuration of the $(+)[\text{Co}(\text{+pn})_3]^{3+}$ ion has demonstrated that another method exists, by which the absolute configuration of both diamines and the complexes of these diamines can be obtained. We have therefore developed this method. We have relied heavily on the experimental results of previous workers. Most of these results were obtained before the second World War but they are nevertheless reliable. The earlier

workers assigned the configurations of the metal complexes with theories, which have since been shown to be unreliable. We have therefore used their experimental results and modern theories to assign the absolute configurations.

Modern theory can be summarised in the following statements:

- 1) The trisdiamine complexes of metals will have at equilibrium a favoured isomer.
- 2) Diamines with the same absolute configuration will produce $[\text{metal}(\text{diamino})_3]^{3+}$ ions with the same configuration. The Cotton effects of these ions will be identical with each other and the Cotton effects for the enantiomer of $[\text{Coen}_3]^{3+}$ with the same configuration.
- 3) It is assumed that the components of the absorption bands in these ions are placed in the same order.

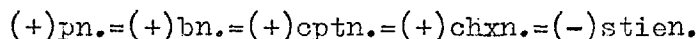
The absolute configurations of (+)propylenediamine⁽⁵⁸⁾ and (+)butane-2,3-diamine⁽⁵⁹⁾ have been assigned by chemical correlations. It has been shown⁽⁶⁰⁾ from Drude plots of rotatory dispersion data that the absorption band of diamines at about 230 mμ is optically inactive. The Cotton effects of the diamines therefore lie outside the region, which can be examined by modern spectropolarimeters. When the diamine forms a chelate ring with a transition metal the d-d transitions of the metal become optically active by asymmetric induction from the ligand.

We have studied six diamines, which for convenience we will abbreviate as follows: pn, 1,2-diaminopropane; bn, 2,3-diaminobutane; cptn, trans-1,2-diaminocyclopentane; chxn, trans-1,2-diaminocyclohexane; stien, 1,2-diamino-1,2-diphenylethane; phenen, phenylethylenediamine.

Corey and Bailar used the known absolute configuration⁽⁵⁹⁾ of (+)bn. to predict that the most stable isomer of $[\text{Co}(+\text{bn})_3]^{3+}$ should be dextrorotatory at the Na_D line. This is just another way of saying that this isomer will have the same configuration as the most stable isomer of $[\text{Co}(+\text{pn})_3]^{3+}$, that is the D configuration. The O.R.D. of this isomer has been measured⁽⁶¹⁾ and it is identical with that of $(+)\text{[Coen}_3\text{]}^{3+}$. This confirms the absolute configuration of (+)bn. and Corey and Bailar's prediction. Corey and Bailar also predicted the absolute configuration of (-)cptn. from the sign of the rotation of the trisdiamine complex of cobalt. However the O.R.D. curve of $(+)\text{[Co}(-\text{cptn})_3\text{]}^{3+}$ is the mirror image of that of $(+)\text{[Coen}_3\text{]}^{3+}$. The sign of the rotation of the two complexes happened to be positive in both cases. This is a good example of the futility of comparing configurations by the sign of the optical rotation at one wavelength. It is essential that the optical activity of the compounds is studied over as large a spectral range as possible and especially in the regions, where the Cotton effects

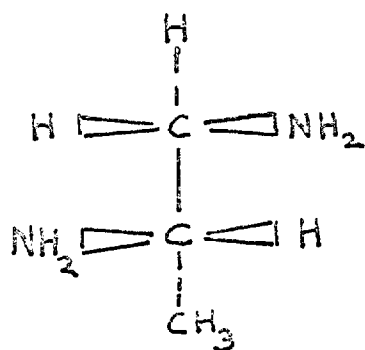
are to be found.

The absolute configuration of (+)chxn. can be found from the O.R.D. of $(-)[Co(+chxn)_3]^{3+}$, which is the most stable isomer of $[Co(+chxn)_3]^{3+}$. The O.R.D. curve⁽⁶²⁾ of this isomer is very similar to that of $(+)[Co(+pn)_3]^{3+}$. Therefore (+)chxn. has the same absolute configuration as (+)pn. We have prepared $(-)[Cr(-pn)_3]^{3+}$. The O.R.D. curve of this ion is the mirror image of the O.R.D. curve⁽⁶²⁾ of $(+)[Cr(+chxn)_3]^{3+}$. This is further confirmation of the configuration of (+)chxn. Gillard⁽⁶³⁾ has pointed out that the O.R.D. curve⁽⁶⁴⁾ of the most stable isomer of $[Co(-stien)_3]^{3+}$ is ~~the mirror image of~~ ^{similar to} $(+)[Co(+pn)_3]^{3+}$ and so (-)stien. has the same absolute configuration as (+)pn. Therefore from stereospecific arguments the configurations of the diamines are related thus:

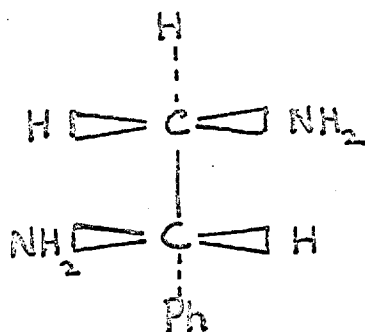


This relationship is supported⁽⁶⁰⁾ by the O.R.D. curves of (+)pn., (+)cptn. and (+)chxn. in the visible region, which are all plain and positive. The absolute configurations of these diamines and of (+)phenen., which was assigned by Gillard⁽⁶³⁾, are shown in Figure 4.

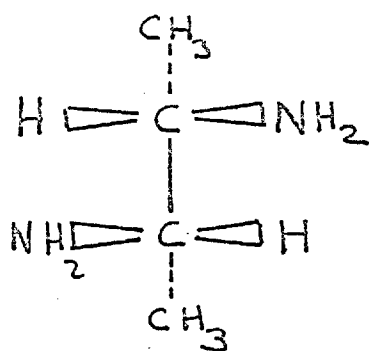
The assignments are reinforced by the study of the Cotton effects of other metal complexes. It has been observed⁽⁶³⁾ that the O.R.D. curves of $[Ni(+bn)_3]^{2+}$ and of $[Ni(-pn)_3]^{2+}$ are



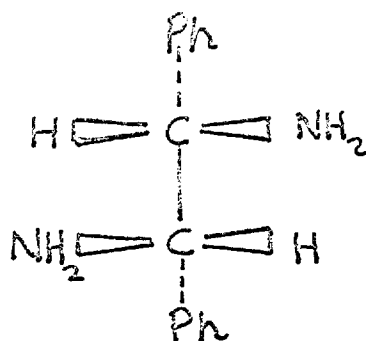
(+)pn



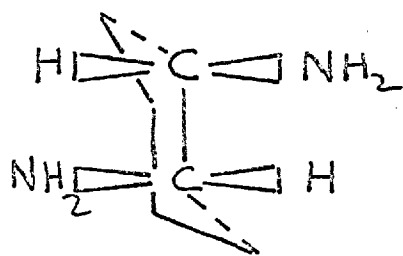
(+)phenen



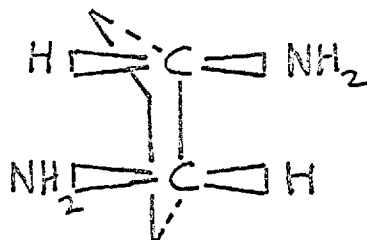
(+)bn



(-)stien



(+)chxn



(+)cptn

Figure 4.

Absolute configurations of diamines.

enantiomorphous. The O.R.D. curve of $[\text{Ni}(-\text{stien})_3]^{2+}$ has also been published⁽⁶⁴⁾. It is approximately the mirror image of that of $[\text{Ni}(-\text{pn})_3]^{2+}$ ⁽⁶¹⁾. However these complexes are not very suitable for a comparison as the range, over which the O.R.D. was measured contained no spin-allowed electronic transitions. The Cotton effects of these complexes are just outside this region. The diamine-N, -N, -N', -N', -tetra-acetic acids can be used to compare configurations. The disodium salts of these acids form very stable cobalt(III) complexes. It has been shown⁽⁶⁵⁾⁽⁶⁶⁾ that these complexes are absolutely stereospecific. McDermott and Sargeson⁽⁶⁶⁾ have shown that the O.R.D. curves of the cobalt(III) complexes of the acids made from (-)chxn. and (-)pn. are equivalent. This confirms the previous assignment⁽⁶⁷⁾ of the absolute configuration of (+)chxn.

The trans-dichlorobisdiaminecobalt(III) complexes can also be used to compare configurations. These complexes are not asymmetric. The Cotton effects, which are observed, are produced by the vicinal action of the asymmetric atoms in the ligands. Figure 5 shows the O.R.D. curve of (-)trans $[\text{Co}(-\text{cptn})_2\text{Cl}_2]^+$ ⁽²⁹⁾ and the O.R.D. curve of (-)trans $[\text{Co}(-\text{pn})_2\text{Cl}_2]^+$, which we prepared. Gillard⁽⁶³⁾ has observed that the O.R.D. curves of (-)trans $[\text{Co}(-\text{phenen})_2\text{Cl}_2]^+$ and (-)trans $[\text{Co}(-\text{stien})_2\text{Cl}_2]^+$ are enantiomorphous. We prepared (-)trans $[\text{Co}(-\text{stien})_2\text{Cl}_2]\text{Cl}$ and

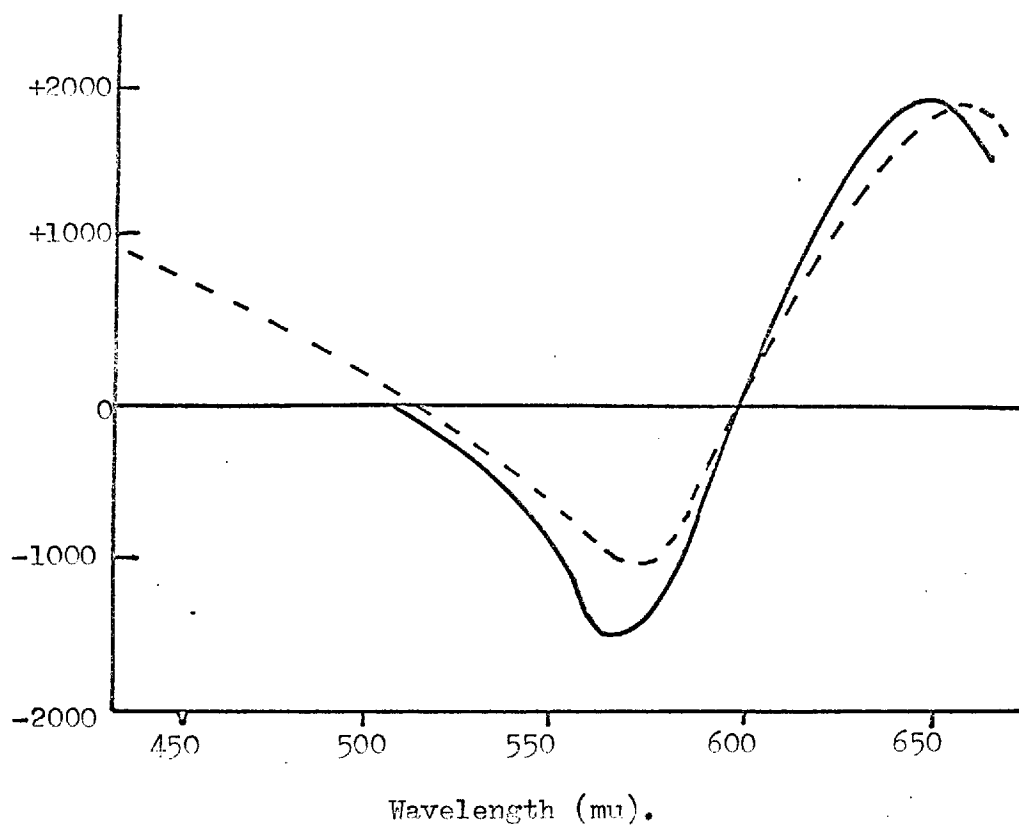


Figure 5. O.R.D. curves of $(-)\text{trans}[\text{Co}(-\text{AA})_2\text{Cl}_2]\text{Cl}$.

Full line: $(-)\text{trans}[\text{Co}(-\text{cptn})_2\text{Cl}_2]\text{Cl}$.

Broken line: $(-)\text{trans}[\text{Co}(-\text{pn})_2\text{Cl}_2]\text{Cl}$.

compared the circular dichroism of this compound with the circular dichroism of $(-)\text{trans}[\text{Co}(-\text{pn})_2\text{Cl}_2]\text{Cl}_2$. They are enantiomorphous. This is shown in Table 4.

Table 4

Circular dichroism of $\text{trans}[\text{Co}(\text{diamine})_2\text{Cl}_2]\text{Cl}$ complexes.

Complex	Position and sign of circular dichroism maxima
$(-)\text{trans}[\text{Co}(-\text{pn})_2\text{Cl}_2]\text{Cl}$	608 mu (+) 464 mu (-)
$(-)\text{trans}[\text{Co}(-\text{stien})_2\text{Cl}_2]\text{Cl}$	610 mu (-) 460 mu (-)

Note. It is the sign of the $E \leftarrow A$ transition at about 600 mu that is significant.

The bisdiamine complexes of copper(II) and nickel(II) may also be used to compare the configurations of diamines. Gillard⁽⁶³⁾ used the copper(II) complexes of $(-)\text{pn}$. and $(-)\text{chxn}$. We have prepared the nickel(II) complexes of $(+)\text{pn}$. and $(-)\text{stien}$. These complexes are named after Lifschitz, who first studied their interesting spectral and magnetic properties⁽⁵⁰⁾⁽⁶⁴⁾⁽⁶⁸⁾⁽⁶⁹⁾. In aqueous solution the salts are blue and paramagnetic. The circular dichroism of $[\text{Ni}(+\text{pn})_2](\text{ClO}_4)_2$ showed a negative Cotton

effect at 575 mμ. The O.R.D. curves of $[\text{Ni}(+\text{pn})_2](\text{ClO}_4)_2$ and $[\text{Ni}(-\text{stien})_2]\text{Cl}_2$ ⁽⁶⁴⁾ are exactly parallel. In certain organic solvents, such as nitromethane, these salts are yellow and diamagnetic. We measured the circular dichroisms of $[\text{Ni}(+\text{pn})_2](\text{ClO}_4)_2$ and $[\text{Ni}(-\text{stien})_2](\text{ClO}_4)_2$ in nitromethane. They both showed a negative Cotton effect at 460 mμ. All the evidence which we have collected is in complete agreement as to the absolute configurations of the diamines. The diamines: (+)pn., (+)bn., (+)cptn., (+)chxn., (+)phenen. and (-)stien. all have the same configuration. Each of these diamines will cause the trisdiamine complex of a metal to exist predominantly in the D configuration.

The electronic transitions in the trisdiamine complexes of rhodium(III) are analogous to those in the corresponding cobalt(III) complexes, but they are found in the ultra-violet region of the spectrum because of the greater splitting of the energy levels. The most stable complexes of rhodium(III) with (+)cptn. and (+)chxn. are $(-)[\text{Rh}(+\text{cptn})_3]^{3+}$ and $(-)[\text{Rh}(+\text{chxn})_3]^{3+}$. While these ions must have the D configuration, the O.R.D. curves reported⁽⁶²⁾ do not extend into the ultra-violet region. We have therefore examined the complex of (-)propylenediamine. The most stable isomer of $(+)[\text{Rh}(-\text{pn})_3]^{3+}$, which must have the L, or $\text{R}(\text{C}_3)\text{S}(\text{C}_2)$ configuration from the steric requirements of the

(-)-pn., has a negative circular dichroism band at 365 mμ.
 (-)[Rh(en)₃]³⁺ shows a positive circular dichroism band at 310 mμ and so is of the opposite configuration to (+)[Rh(-pn)₃]³⁺, i.e. it is D(-)[Rh(en)₃]³⁺. The circular dichroisms of these two ions are shown in Figure 6.

Chromium(III) also forms tris-complexes with diamines. With (-)-pn. the most stable isomer is (-)[Cr(-pn)₃]³⁺, whose absolute configuration is known from the steric requirements of the diamine to be L, Δ or R(C₃)S(C₂). The circular dichroism of this complex ion, which we prepared is shown in Figure 7 with that of (+)[Cren₃]³⁺ (62). The (+)[Cren₃]³⁺ ion has therefore the D configuration. This confirms our earlier conclusion (70) drawn from the similarity of the O.R.D. curves of D(-)[Cr(+chxn)₃]³⁺ and (+)[Cren₃]³⁺. The O.R.D. curve (61) of (-)[Crtn₃]³⁺, where tn. is propane-1,3-diamine, is parallel to that of (+)[Cren₃]³⁺ and it may be assigned as D(-)[Crtn₃]³⁺. The ions (+)[Cren₃]³⁺, (-)[Crtn₃]³⁺, (-)[Cr(+chxn)₃]³⁺ and (+)[Cr(+pn)₃]³⁺ have therefore the D configuration.

The electronic transitions of the spin-paired ground state d⁶ complexes for O_h and D₃ symmetry were described in chapter I. Chromium(III) has a spin-free ground state d³ electronic configuration. The electronic transitions are completely analogous with the d⁶ configuration. This is shown in Table 3 in

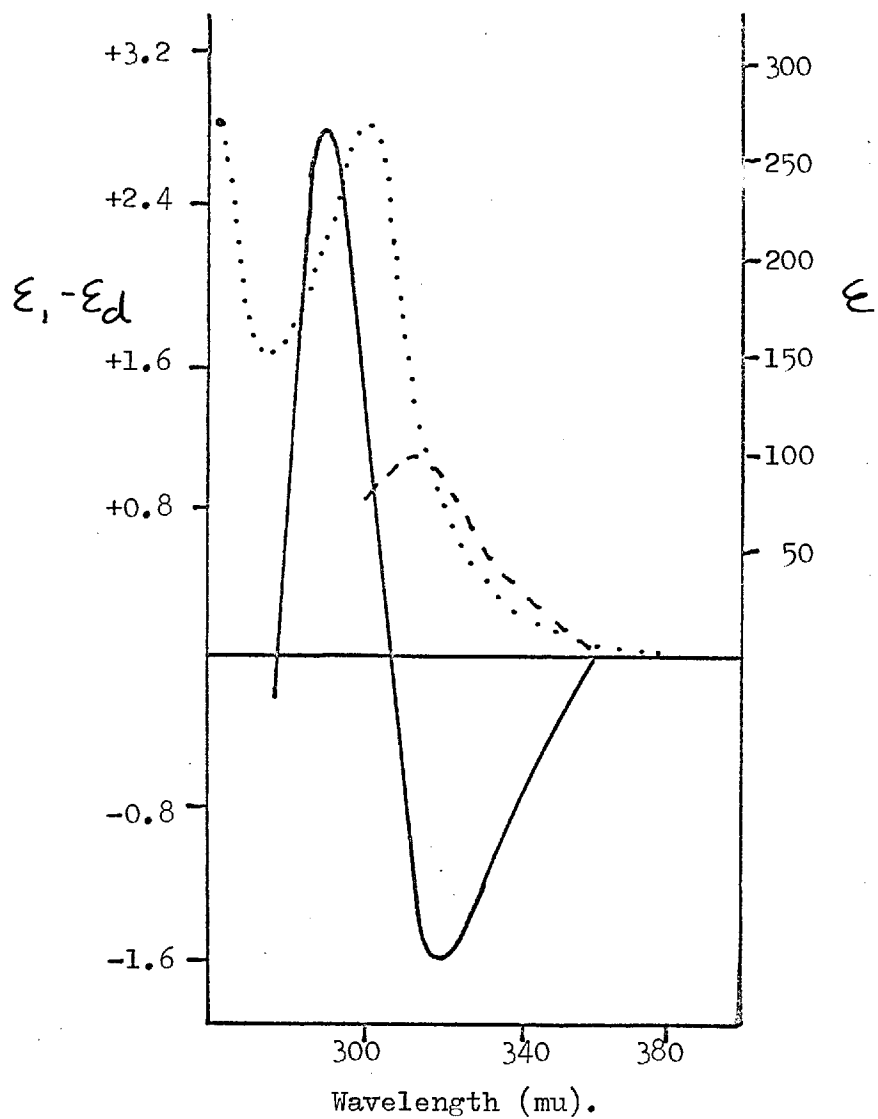


Figure 6. Circular dichroisms of $[Rh(AA)_3]I_3 \cdot 2H_2O$.

Full line: $L(+)[Rh(-pn)_3]I_3 \cdot 2H_2O$.

Broken line: $D(-)[Rh(en)_3]I_3 \cdot 2H_2O$.

Dotted line: Absorption spectrum of
 $[Rhpn_3]I_3$.

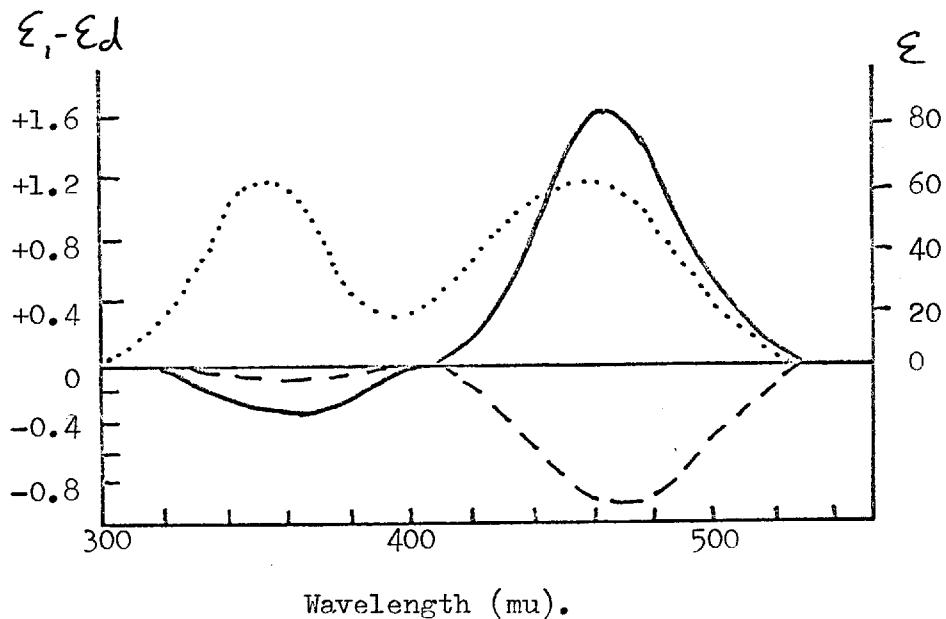


Figure 7.

- Circular dichroism of (+)[Cren₃]³⁺.
- - - - - Circular dichroism of (-)[Cr(-pn)₃]³⁺.
- Absorption spectrum of [Cren₃]³⁺ (that of
[Crpn₃]³⁺ is extremely similar).

Chapter I. In both electronic configurations only the first absorption band is magnetic-dipole allowed in O_h symmetry. It has been said⁽¹⁷⁾⁽⁷¹⁾, that in cases where only a single circular dichroism band appears under Band I, owing to the small splitting of the E and the A components, the circular dichroism under that band has the sign of the rotational strength of the E component. The domination of the circular dichroism by the $E \leftarrow A$ transition is shown in the circular dichroisms of both $(+)[Cr(+pn)_3]^{3+}$ and $(+)[Rh(-pn)_3]^{3+}$ (see Figures 6 and 7). The circular dichroism of the trispropylenediamine complexes of cobalt(III), rhodium(III) and chromium(III) are compared in Table 5.

We have shown by arguments based on stereospecificity that $(+)[Cr(+pn)_3]^{3+}$ and $(-)[Rh(+pn)_3]^{3+}$ have the D configuration. It should be noted that the $E_g \leftarrow A_g$ transition in both of these complexes is positive. This confirms Mason's statement⁽¹³⁾ that dihedral d^3 and d^6 complexes have the same absolute configuration as $(+)[Coen_3]^{3+}$ if the spin-allowed transition with lowest energy has an E component with a positive rotatory power. The size of the circular dichroism bands under Band I and Band II is a striking demonstration of the selection rules of Moffitt⁽²⁴⁾. The circular dichroism under Band I is considerably larger than the circular dichroism under Band II. This suggests that the rotational strength of the electronic transitions is controlled by the

Table 5.

Circular dichroism spectra of tris(+)propylenediamine complexes of

Co(III), Rh(III), and Cr(III) (λ in m μ)

Complex	Band I					Band II			Ref.
	$E_a \leftarrow A$			$A \leftarrow A$		$E_b \leftarrow A$			
	$\lambda_{abs}^{(a)}$	$\lambda_{cd}^{(b)}$	$(\epsilon_1 - \epsilon_d)$	λ_{cd}	$(\epsilon_1 - \epsilon_d)$	λ_{abs}	λ_{cd}	$(\epsilon_1 - \epsilon_d)$	
(+)Co(+)pn ₃ ³⁺	470	496	+ 1.9	441	- 0.5	350	346	+ 0.27	70
(+)Cr(+)pn ₃ ³⁺	457	470	+ 0.9	0	0	350	350	+ 0.3	72
(-)Rh(+)pn ₃ ³⁺	301	312	+ 0.5	290	- 0.8	250	0	0	70

0 signifies: not observable. (a), Absorption maximum (b), Circular dichroism maximum

selection rules for O_h symmetry.

In Table 6 some properties of the tris-complexes of inactive diamines are listed. The sign of the optical rotation at the Na_D line does not compare well with the sign of the circular dichroism band under Band 1. This confirms the point that the sign of rotation at a single wavelength is of no value for the comparison of configurations. However the sign of the rotation at the Na_D line of the cation, which gives the less soluble diastereoisomer with the listed anions compares well with the sign of the rotation of the cation, which has the D configuration. The conclusions reached from the solubility criterion are therefore consistent with the configurations of these ions which have been obtained from a study of their Cotton effects. The method of active racemates also compares the relative configurations of the ions correctly.

Table 6

Configurations of trisdiamine complexes.

Cation	D confign. ^(a)	(+)Tartrate	(+)Nitro- camphor	Active Racemates	Circular Dichroism (mμ)	$\xi_1 - \xi_d$
$[\text{Coen}_3]^{3+}$	(+)	(+) ⁽⁷³⁾	unknown	(+) ⁽⁷⁶⁾	493	+ 1.9
$[\text{Rhen}_3]^{3+}$	(-)	(-) ⁽⁴⁸⁾	(-) ⁽²⁸⁾	(-) ⁽⁷⁶⁾	310	+ 1.4
$[\text{Iren}_3]^{3+}$	(-)	unknown	(-) ⁽⁷⁴⁾	unknown	315	+ 0.4
$[\text{Cren}_3]^{3+}$	(+)	unknown	(+) ⁽⁷⁵⁾	unknown	460	+ 1.7

(a) This work.

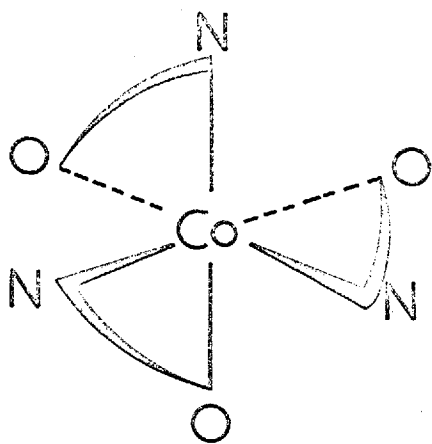
CHAPTER III

TRISAMINO-ACIDATE AND TRISFORMYLCAUPHOR COMPLEXES

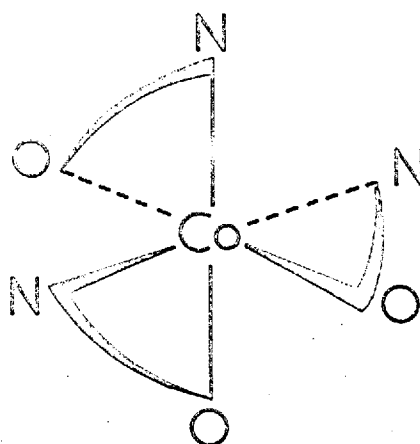
OF COBALT(III) AND RHODIUM(III)

PART I. METAL(AMINO-ACIDATE)₃ COMPLEXES

When three molecules of an amino-acid form a complex with a metal of octahedral stereochemistry, two geometrical isomers are possible (see Figure 8). The two isomers of $\text{Co}(\text{glycinate})_3$ are readily separable⁽⁷⁷⁾ through their different solubilities in water. The red β -isomer is insoluble in water, the violet α -isomer is more soluble in water. The assignment of structure to the two geometrical isomers has relied⁽⁷⁸⁾⁽⁷⁹⁾ on their different symmetries. The β -isomer belongs to the C_3 point group, while the α -isomer belongs to the C_1 point group. The selection rules for magnetic-dipole transitions in these two point groups are given in Table 3. Since the electronic spectrum of the α -isomer shows greater splitting for the longest wavelength absorption band, (Band 1), than does the spectrum of the β -isomer, the (1,2,6) structure was assigned to the α -isomer and the (1,2,3) structure was assigned to the β -isomer⁽⁷⁸⁾. In a similar way the infra-red spectrum of the α -isomer shows ~~more~~ ^{less} degeneracy than the spectrum of the β -isomer⁽⁷⁹⁾. The visible and infra-red spectra of the $\text{Co}(\text{L-alaninate})_3$ isomers are very similar to the corresponding isomers of $\text{Co}(\text{glycinate})_3$. Figure 9 compares the electronic spectra.



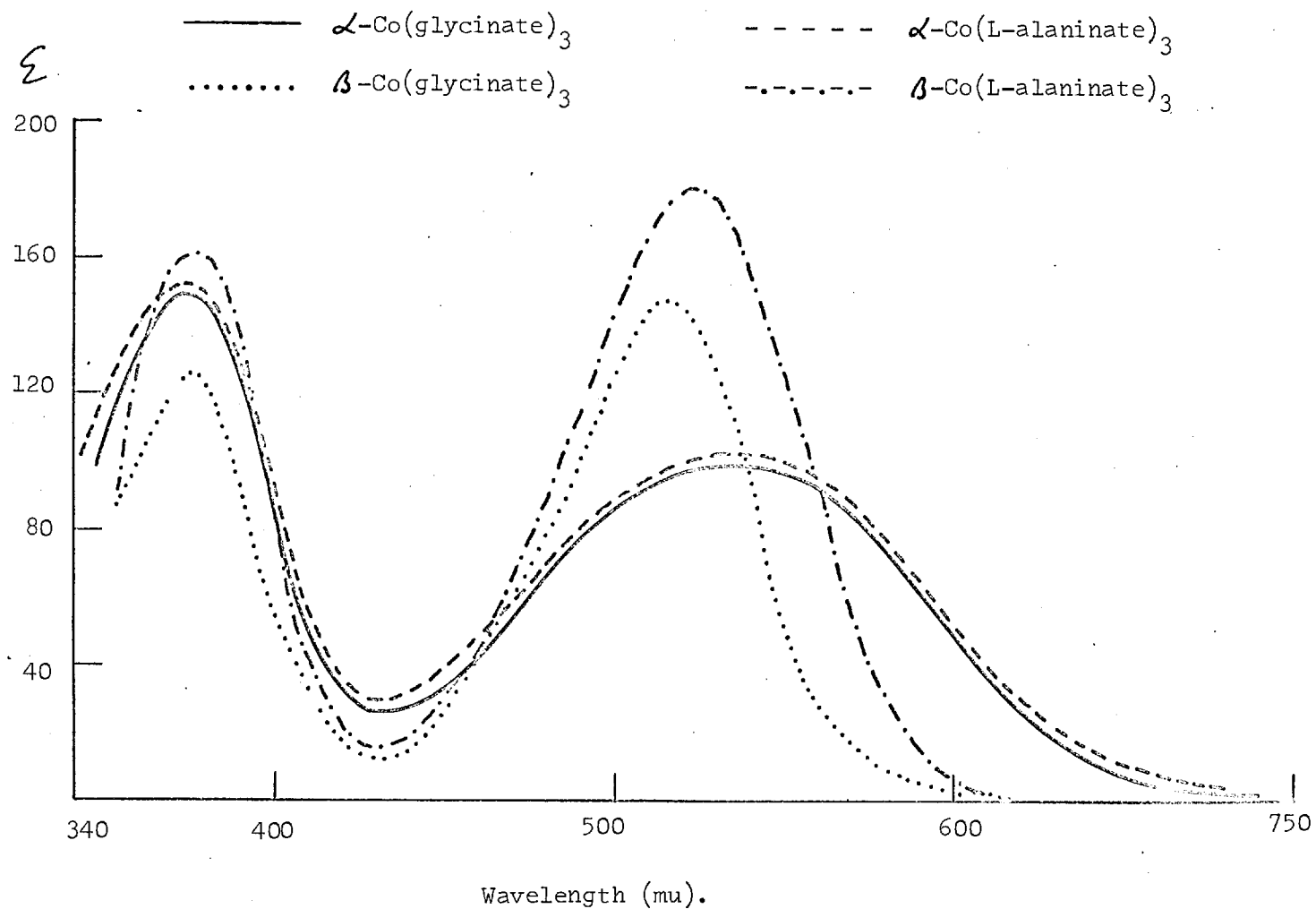
β , cis-cis or
1,2,3 isomer



α , cis-trans or
1,2,6-isomer

Figure 8. The geometrical isomers of $\text{Co}(\text{glycinate})_3$.

Figure 9. The electronic spectra of $\text{Co}(\text{glycinate})_3$ and $\text{Co}(\text{L-alaninate})_3$ isomers.



The original method⁽⁷⁷⁾ for the preparation of the geometrical isomers of the cobalt(III) complexes has recently been improved⁽⁸⁰⁾. We have now prepared the isomers of trisL-alaninatorrhodium(III) by the reaction of hydrated rhodium(III) oxide with L-alanine. The isomers were separated in the same way as for the cobalt(III) isomers; the $\beta(-)$ -isomer is extremely insoluble in water, the $\beta(+)$ -isomer is sparingly soluble in water, while the α -isomers are readily soluble in water. Both β -isomers are off-white, anhydrous compounds; their electronic spectra are similar (see Figure 10). The O.R.D. curve of the $\beta(-)$ complex of rhodium(III) is similar in form to that of the $\beta(+)$ complex of cobalt(III). The O.R.D. curves of the $\beta(+)$ complex of rhodium and the $\beta(-)$ complex of cobalt are also similar. The infra-red spectra of the α and β -isomers confirm the assignments given. Details of the infra-red spectra are given in the Experimental Section. X-ray powder photographs of the two β trisalaninatorrhodium(III) isomers confirmed their similar structure. The solubility relationship between the β -isomers of the rhodium(III) complex is not the same as with the β -isomers of the analogous cobalt(III) complex. By continued fractionation of the more soluble complex, α -isomers are obtained, which are characterised by their analyses (monohydrated) and their infra-red spectra. In this case, the small amplitude of the Cotton effects suggests that the compound obtained was a mixture

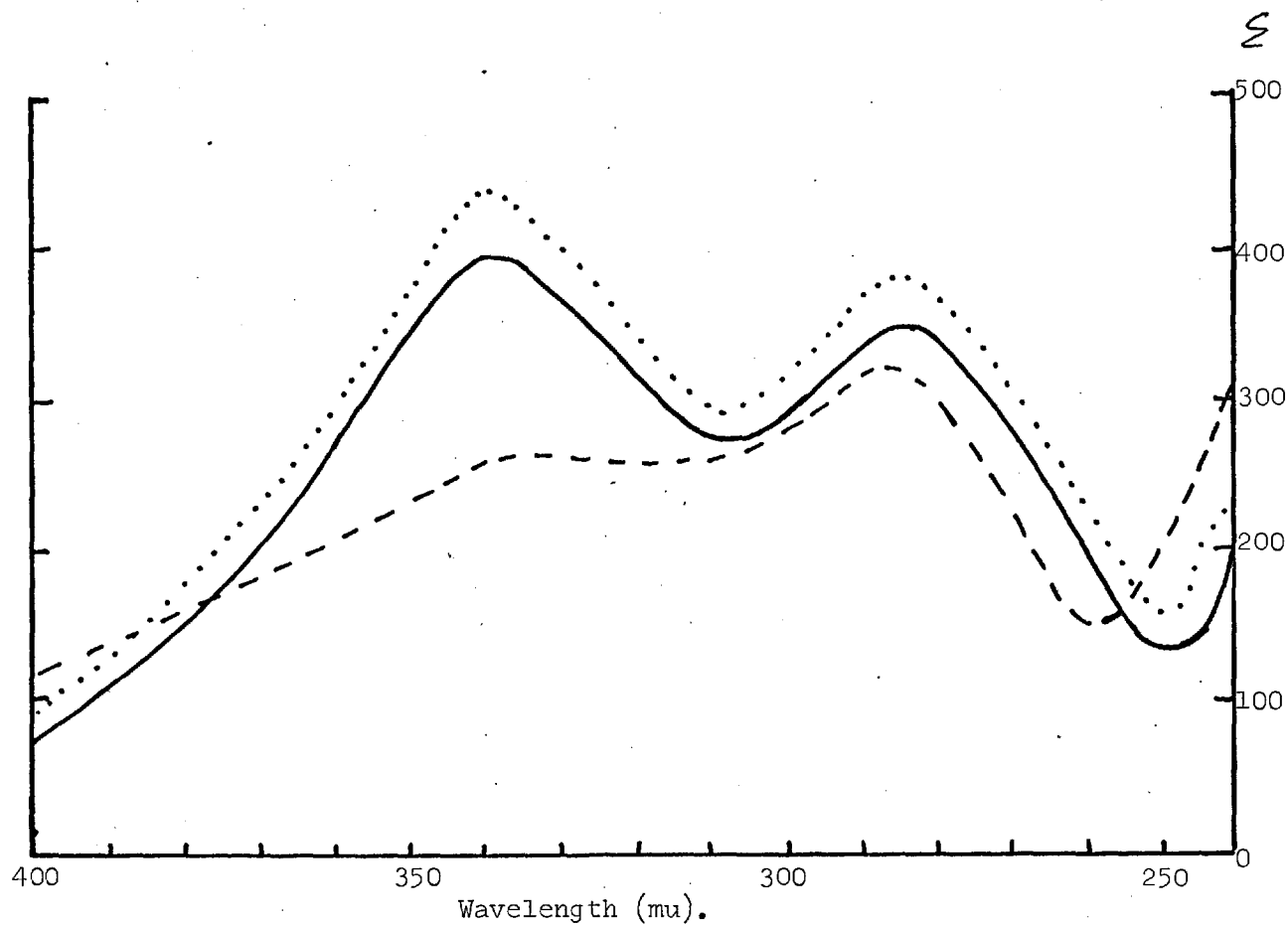


Figure 10. The electronic spectrum of α and β -isomers of $\text{Rh}(\text{L-alaninate})_3$

Full line: $\beta(-)\text{-Rh}(\text{L-ala})_3$

Broken line: mixture of α -isomers of $\text{Rh}(\text{L-ala})_3$

Dotted line: $\beta(+)\text{-Rh}(\text{L-ala})_3$

of the $\alpha(+)$ and the $\alpha(-)$ -isomers.

Both α and β -isomers of $M(\text{amino-acidate})_3$ are resolvable, as shown in Figure 11. The further optical isomerism arising from any asymmetry, which may be present in the ligand is considered later. We denote their absolute configurations as shown because left-handed helicity about the three-fold axis is characteristic of $D(+)[\text{Coen}_3]^{3+}$. It might also be called $S(C_3)$ or Λ . By analogy, the α -isomers are called D and L. The optical isomerism in $M(\text{amino-acidate})_3$ complexes was demonstrated by the resolution⁽⁸¹⁾ of the $DL\alpha$ and the $DL\beta$ -isomers of $\text{Co}(\text{glycine})_3$ on a starch column. In this case the stabilities of $D\alpha$ and $L\alpha$ -isomers are equal, as are those of $D\beta$ and $L\beta$. However in complexes involving such optically active amino-acids as L-alanine, the $D\alpha$ and $L\alpha$ -isomers are no longer enantiomers but are diastereoisomers, as are $D\beta$ and $L\beta$, and there is now no reason why the stabilities of these pairs should be equal. Lifschitz studied the $\text{Co}(\text{amino-acidate})_3$ complexes with L-alanine⁽⁴⁴⁾⁽⁴⁵⁾, L-aspartic acid⁽⁴⁴⁾⁽⁴⁶⁾ and L-glutamic acid⁽⁴⁷⁾. He claimed to have isolated the $\alpha(+)$, $\alpha(-)$ and $\beta(+)$ -isomers in the case of alanine, the $\alpha(+)$ and the $\alpha(-)$ -isomers in the case of aspartic acid and all four isomers in the case of glutamic acid. (In the absence of information on absolute configurations we will use the signs of rotation at the NaD line to denote isomers) An inspection of the O.R.D. curves

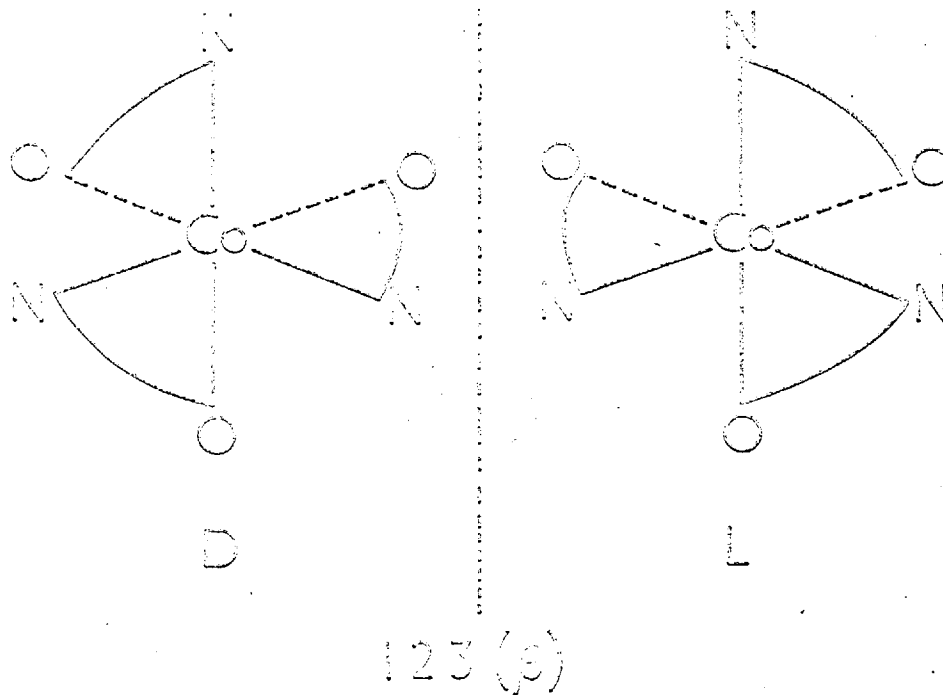
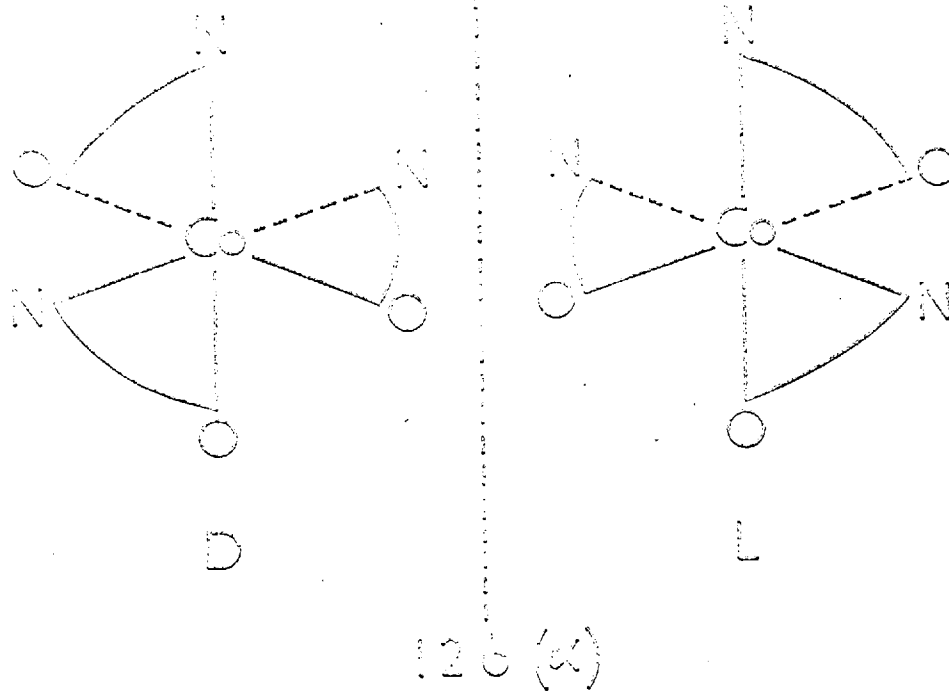


Figure 11.

given for the alanine and glutamic acid complexes suggested that there were inconsistencies.

We have now succeeded in obtaining all four isomers of $\text{Co}(\text{L-alaninate})_3$. The absorption spectra, O.R.D. curves and circular dichroisms are presented in Figures 12-15. The absorption spectra identify the geometrical isomers while the O.R.D. curves distinguish the optical isomers. The three isomers of $\text{Co}(\text{L-alaninate})_3$ described by Lifschitz⁽⁴⁵⁾ are in fact, pure $\alpha(+)$, pure $\beta(+)$ and impure $\alpha(-)$, which he called α' . The O.R.D. curve of this isomer and of the pure $\alpha(-)$ -isomer are compared in Figure 13. The O.R.D. curve of the enantiomer of α -Co(glycinate)₃, which is less adsorbed on a starch column, is shown in Figure 16 with that of $\alpha(+)$ -Co(L-alaninate)₃ for comparison. These two compounds obviously have related geometrical and optical configurations.

The four isomers of $\text{Co}(\text{L-alaninate})_3$ are obtained in the following way: one of the isomers, the red $\beta(+)$, is completely insoluble in water and may thus be separated from the other three, which remain in the violet filtrate. It is believed that this $\beta(+)$ -isomer is optically pure because samples prepared by different methods have identical O.R.D. curves. Further, fractions obtained by dissolving the water-insoluble material in strong sulphuric acid and partially precipitating with water, are again identical. The remaining three isomers were separated by fractional crystallisation.

Figure 12. Properties of $\alpha(+)\text{-Co(L-alanine)}_3$.

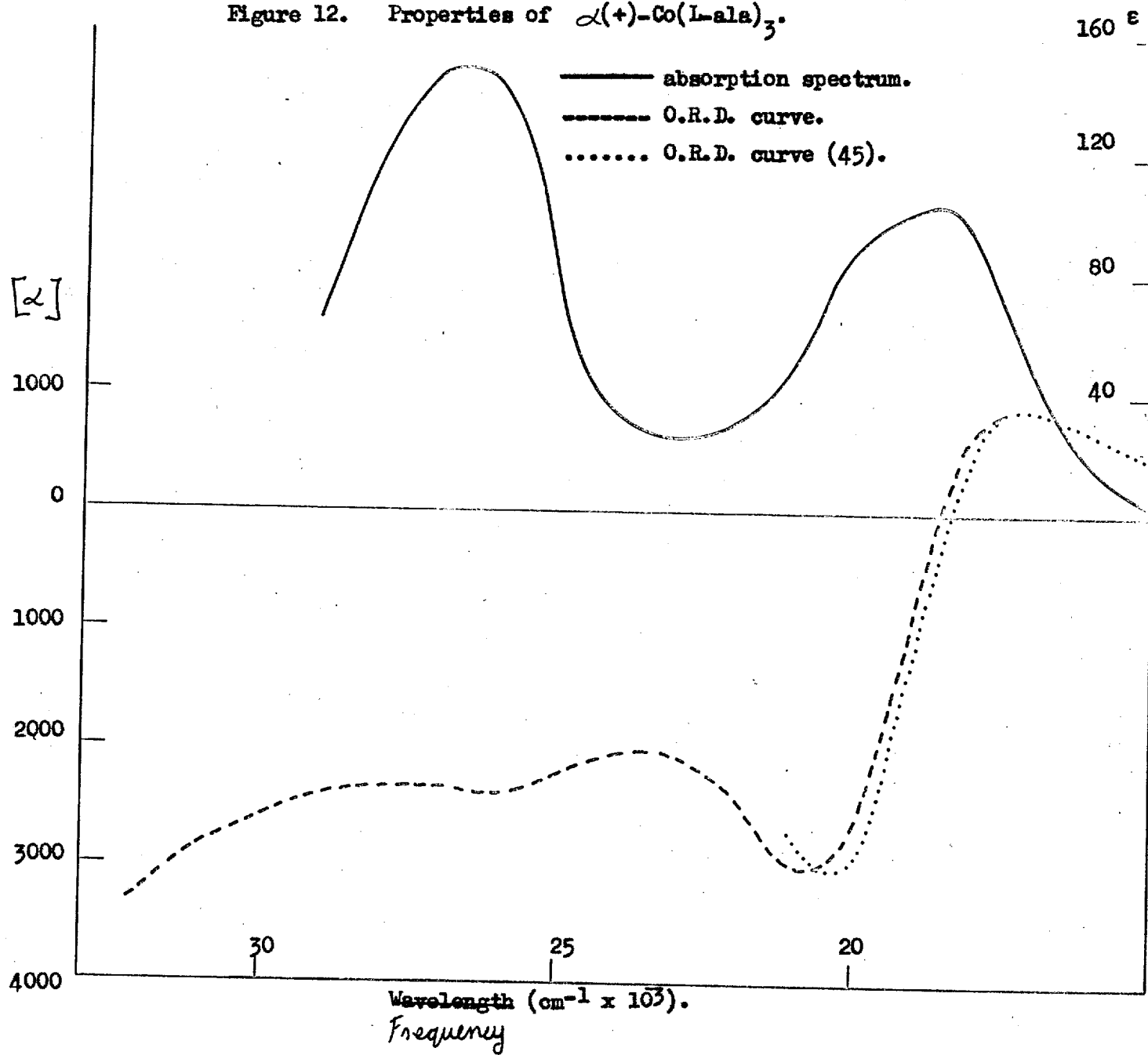


Figure 13. Properties of $\alpha(-)\text{-Co(L-al)}_3$.

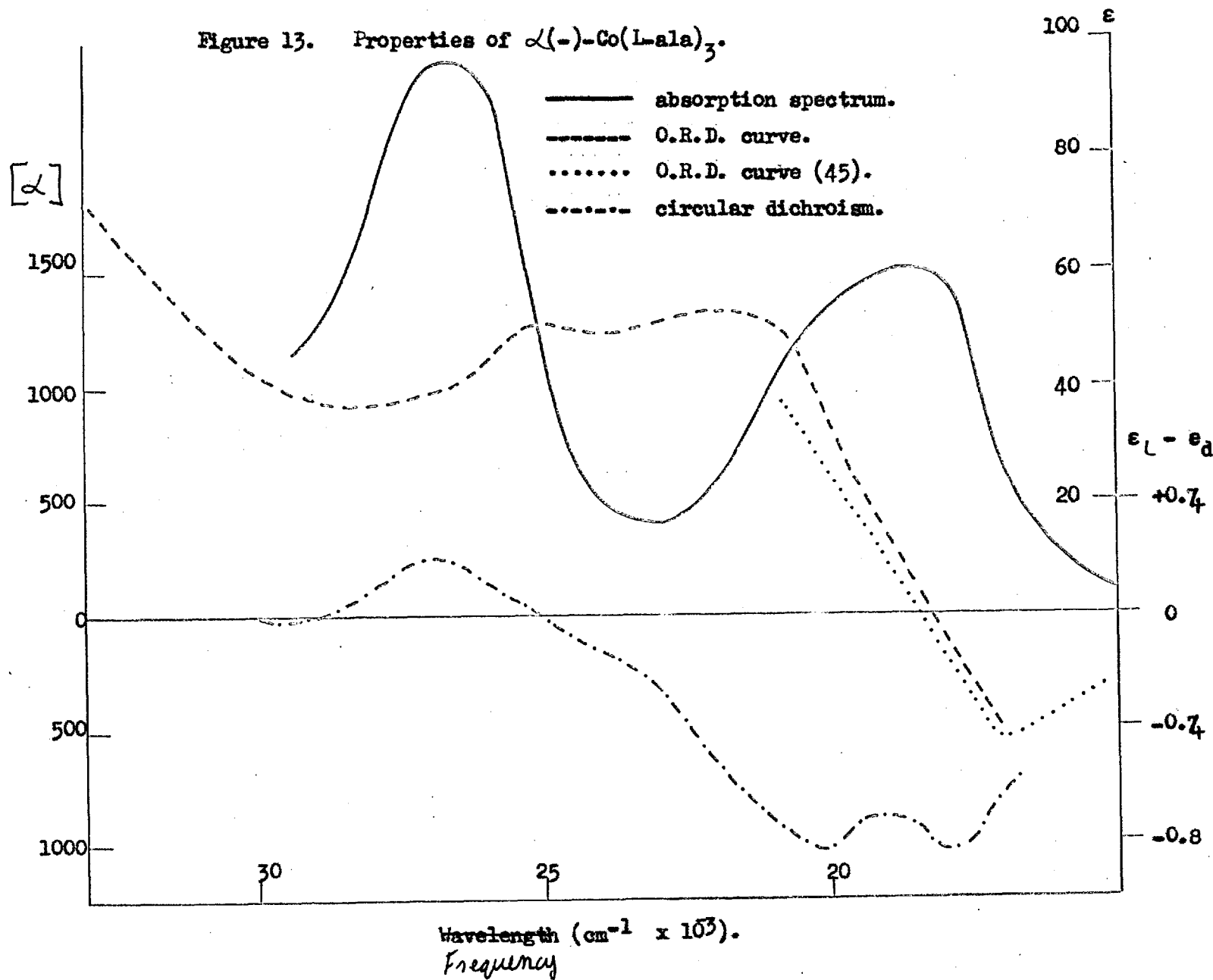


Figure 14. Properties of B(+)-Co(L-al_a)₃.

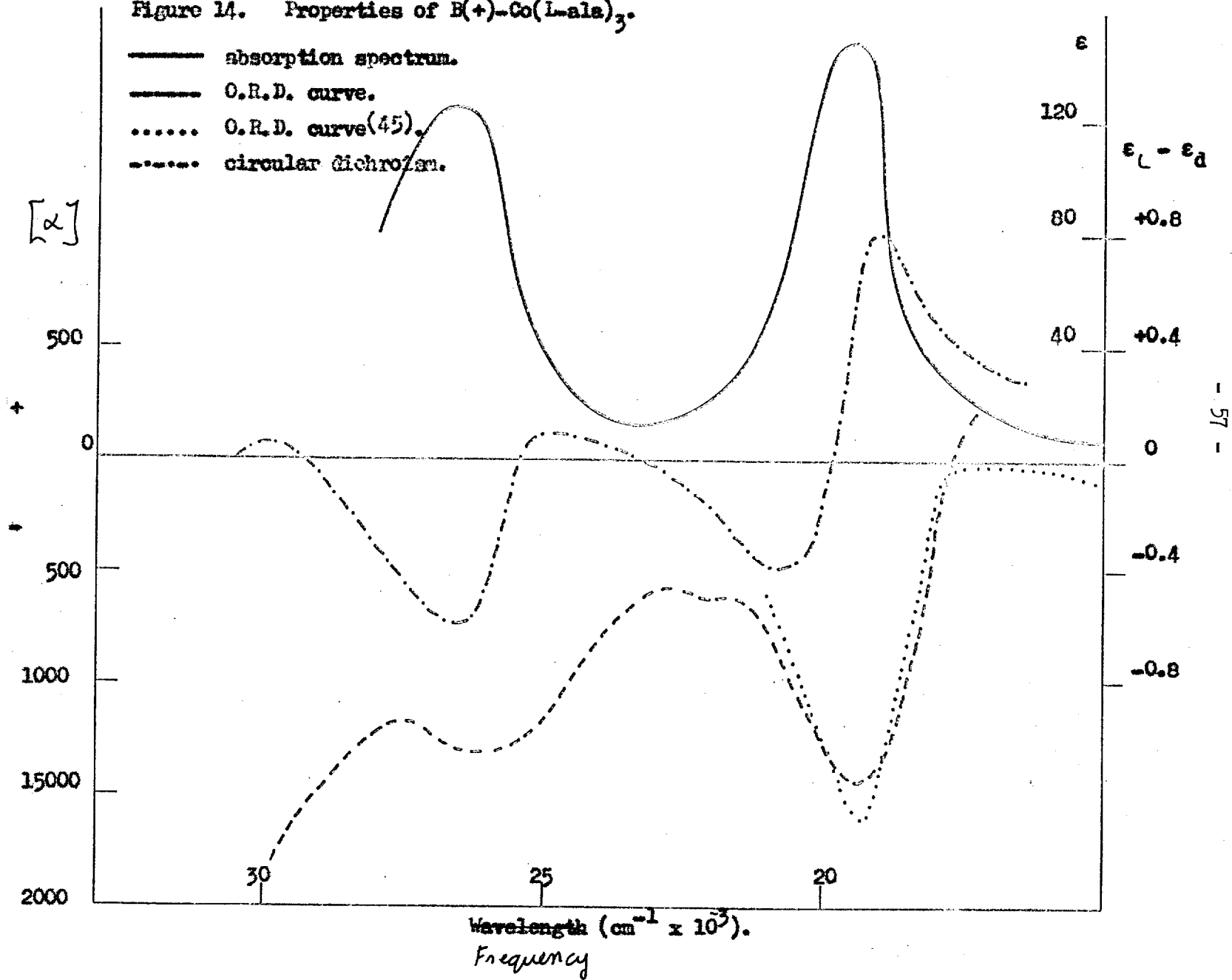


Figure 15. Properties of B(-)-Co(L-al_a)₃.

Full line. absorption spectrum.

Broken line. O.R.D. curve.

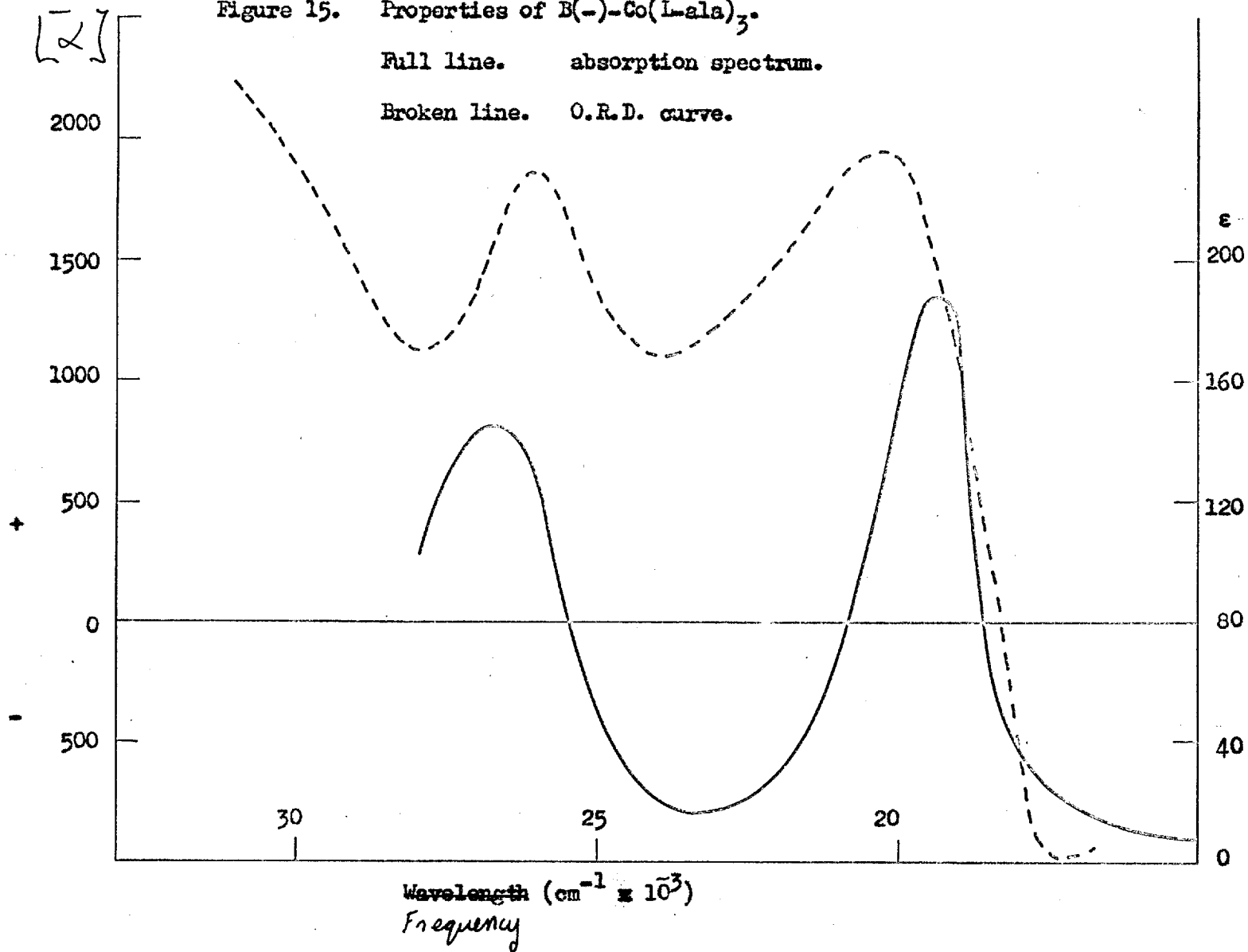
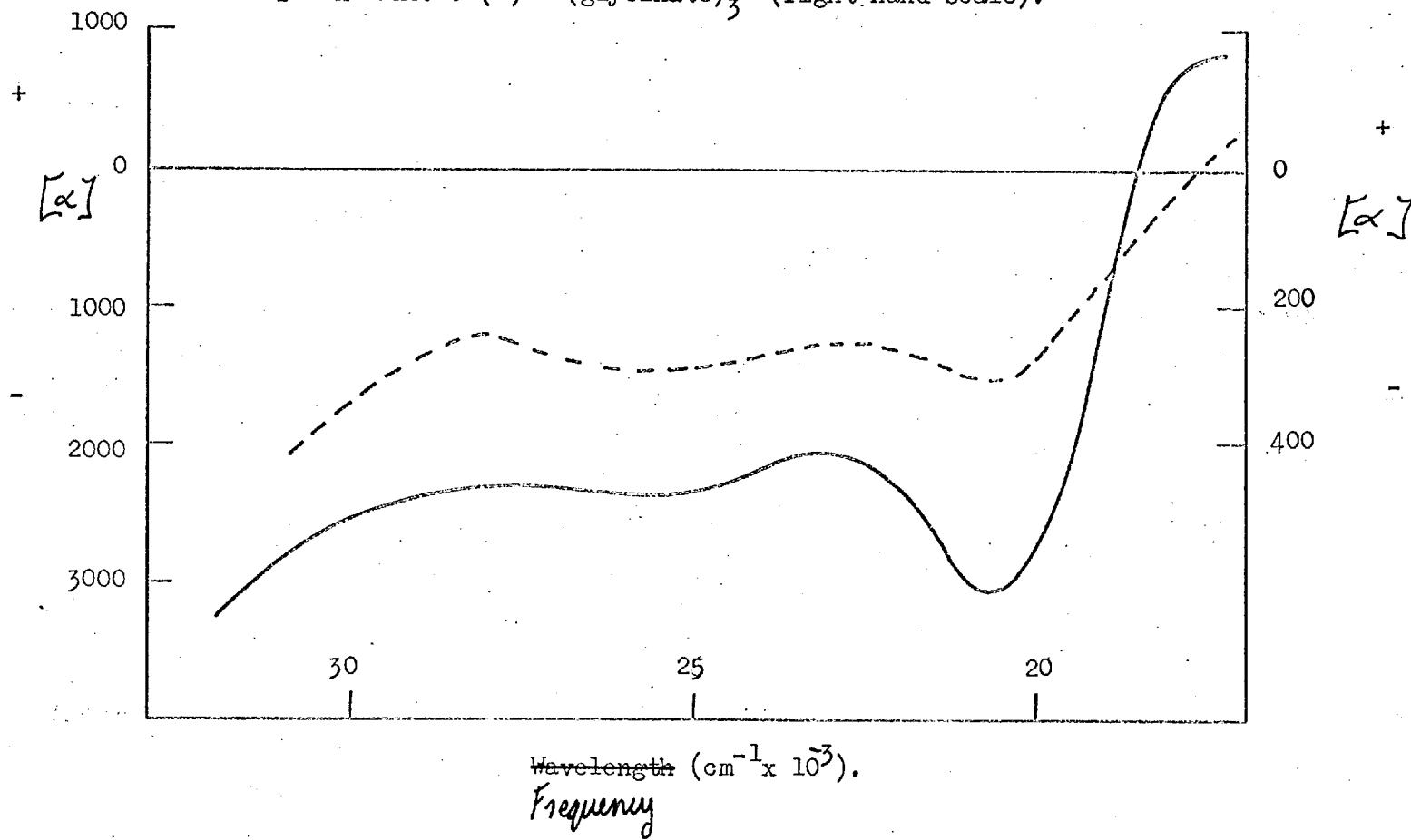


Figure 16. The O.R.D. curves of $\text{Co}(\text{amino-acidate})_3$.

Full line. $\alpha(+)\text{-Co}(\text{l-ala})_3$ (left-hand scale).

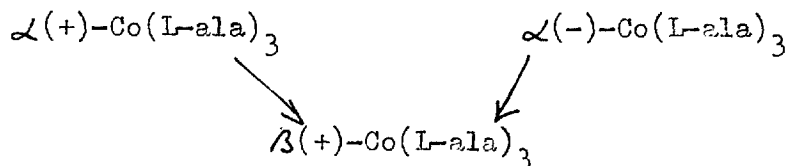
Broken line. $\alpha(+)\text{-Co}(\text{glycinate})_3$ (right-hand scale).



The first four fractions obtained were violet and had very similar rotations. $[\alpha]_{476} = -2750^{\circ}$ (an average value). The sixth fraction, however, had $[\alpha]_{476} = +1190^{\circ}$. The most soluble fraction of all was taken up in aqueous ethanol and chromatographed on alumina, giving an impure violet crop, $[\alpha]_{476} = +623^{\circ}$ and a very small amount of a red isomer, $[\alpha]_{500} = +1700^{\circ}$. Further fractionation of this $\beta(-)$ -isomer did not change its properties. Both the $\alpha(+)$ and $\alpha(-)$ -isomers were recrystallised until a constant specific rotation was obtained. It is believed that all four isomers, which were obtained, are optically pure.

An attempt was made to establish the size of any stereospecific effects in the synthesis of the $\text{Co}(\text{L-alaninate})_3$ isomers by weighing the optically pure isomers. The specific rotations of the optically pure isomers were also used to determine the ratio of the two α -isomers in the reaction product after the β -isomer had been removed. Unfortunately several difficulties arise. The insoluble red $\beta(+)$ -isomer appears to form stereospecifically. This enormous excess of the $\beta(+)$ over the $\beta(-)$ -isomer is probably due not so much to an intramolecular steric effect as to the extremely small solubility of the $\beta(+)$ -isomer displacing the equilibrium completely. This theory is supported by the fact that in attempts to equilibrate either the $\alpha(+)$ or the $\alpha(-)$ -isomer, using active charcoal, the sole product was the insoluble $\beta(+)$ -isomer.

One reaction is of course a complete inversion of optical configuration since the scheme may be written:-



This is the first inversion of configuration in a reaction of any cobalt complex, in which complete inversion has occurred.

Two cases are known, where the crystallisation of one diastereoisomer from a solution, which contains the equilibrium mixture of

diastereoisomers, displaces the equilibrium between the D and the L isomers in solution. The first⁽⁸²⁾ is the resolution of

trisethylenediaminecobalt(III) by (+)tartrate in the presence of cobalt(II) ions. The other case^(43f) is stereospecific preparation of $\text{L}[\text{Co}(-\text{pn})_2\text{CO}_3]\text{I}$ from the DL mixture by slow crystallisation.

The final weights of the two isomers of $\alpha\text{-Co}(\text{L-alaninate})_3$, which were prepared from triscarbonatocobaltate(III) and were separated by fractional crystallisation, were almost equal, the $\alpha(+)$ -isomer being formed in slightly larger amounts than the $\alpha(-)$ -isomer.

However, using the preparation from cobalt(III) oxide, the proportions were reversed. Any stereospecificity is therefore small and variable. The stereospecificity in the β -isomers cannot be determined because of the differences in solubility between the isomers.

The $\alpha(-)$ -isomer of $\text{Co}(\text{glycine})_3$, which had been partly

resolved, was boiled with activated charcoal. The optical activity was lost in two minutes. When the unresolved β -isomer of this complex was boiled with activated charcoal, it was soon completely converted to the α -isomer. This suggests that the amino-acid chelate rings are not as inert as has previously been supposed and also that the α -isomers are more stable than the β -isomers. The complexes of rhodium(III) are more kinetically inert than the analogous complexes of cobalt(III). The stereospecificity of the $\text{Rh}(\text{L-alaninate})_3$ system has been studied. The β -isomers were separated by fractional crystallisation. The O.R.D. curves of the insoluble $\beta(-)$ -isomer from both methods of preparation were identical. This isomer is probably optically pure because of its insolubility. It is suggested that the absolute configuration of this isomer is the same as that of the insoluble $\beta(+)$ -isomer of cobalt(III); this is essentially an application of the method of less soluble diastereoisomers, though the present case is the first application to non-electrolytic complexes. In the case of the soluble isomers, the less soluble fraction, $\beta(+)$, may readily be recrystallised to constant optical rotation, which suggests that our material is optically pure. The mother liquors contain both α -isomers. The small Cotton effects of solids obtained suggests that we have not succeeded in obtaining an optically pure α -isomer, because both are very soluble in water. The O.R.D. curves of the two pairs of analogous complexes are given in Figures 17 and 18.

Figure 17. O.R.D. curves for β -D-M(L-ala)₃.

Full line. $\beta(+)$ -Co(L-ala)₃.

Broken line. $\beta(-)$ -Rh(L-ala)₃.

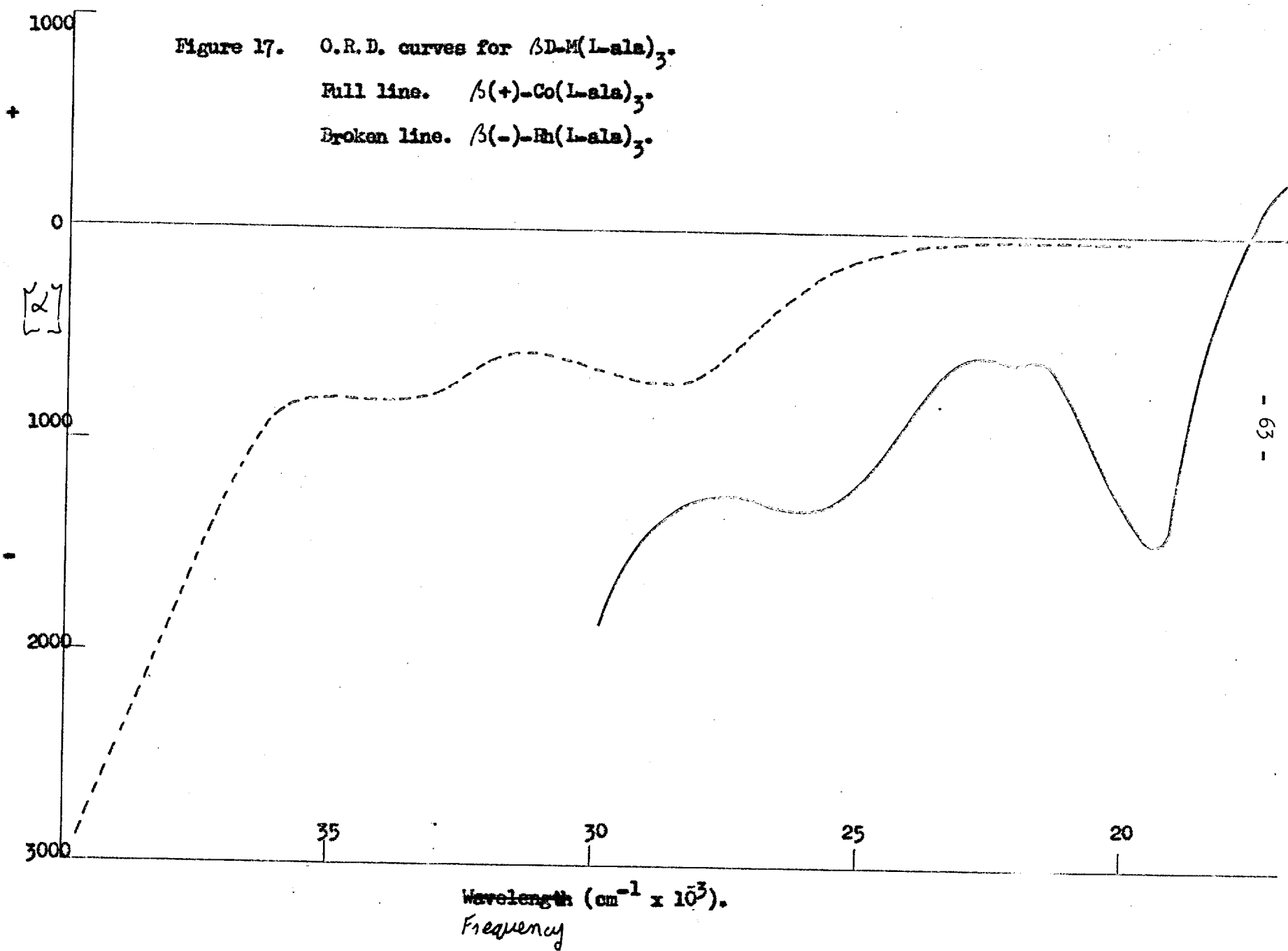
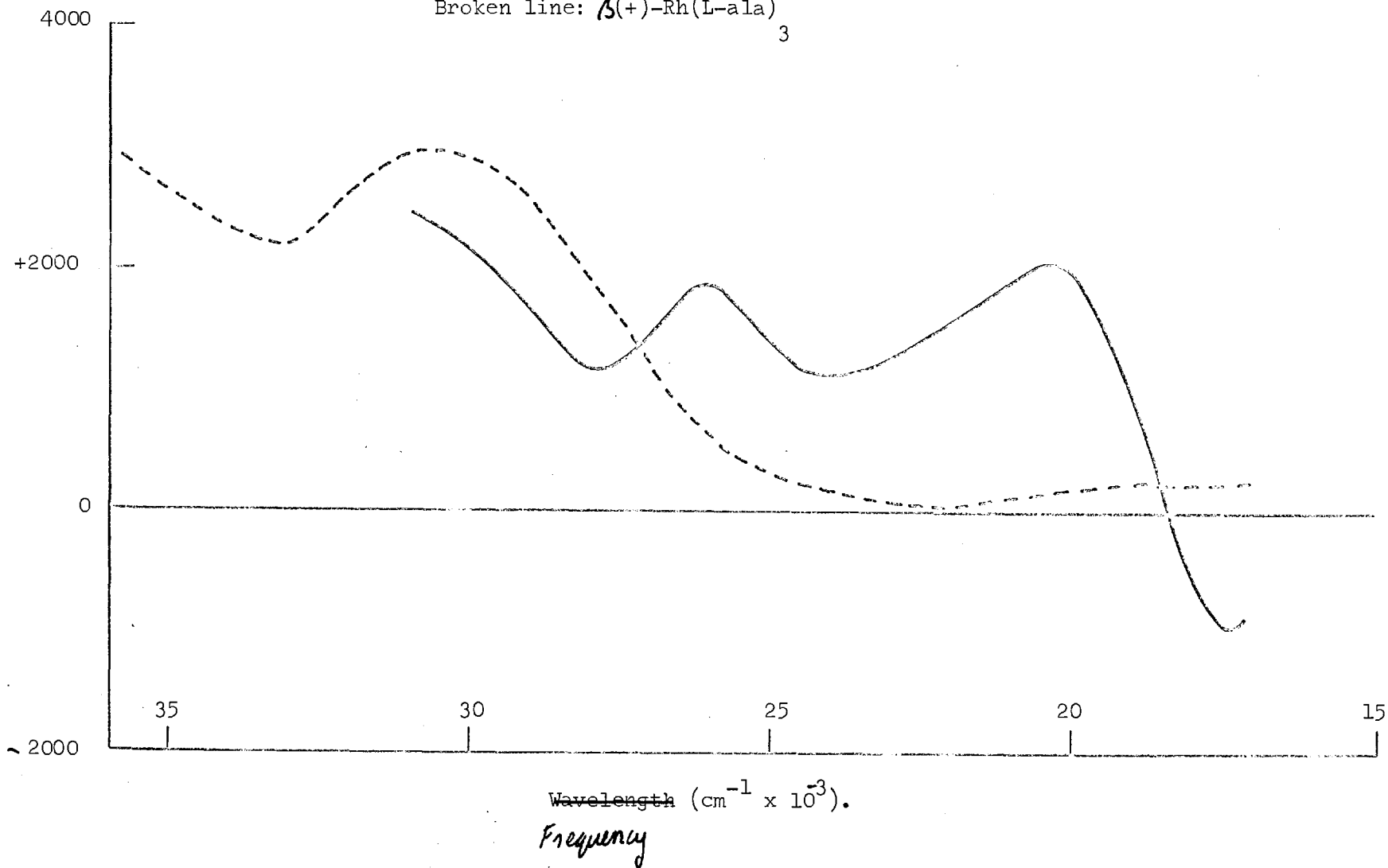


Figure 18. O.R.D. curves for β L-Co(L-ala)₃.

Full line: $\beta(+)$ -Co(L-ala)₃

Broken line: $\beta(+)$ -Rh(L-ala)₃



The circular dichroism results for the $\beta(+)$ -isomer and the $\alpha(-)$ -isomer of $\text{Co}(\text{L-alaninate})_3$ may be interpreted in the light of the symmetries of the complexes. The magnetic-dipole selection rules for the C_1 and C_3 point groups are given in Table 3. The β -isomer has C_3 symmetry and so all four transitions are magnetic-dipole allowed. Four components are therefore expected in the circular dichroism spectrum. Opposite signs of rotational strengths are expected for the two components of Band I, as in the $(+)[\text{Coen}_3]^{3+}$ ion. From Figure 14 it is clear that this expectation is borne out. For Band II the rather large rotational strength of the negative component at 368 m μ may be attributed to intensity borrowing from the charge transfer transition with a negative Cotton effect at 220 m μ . An interesting point is that a third component is just apparent under Band II. This may be due to the presence of some species of symmetry lower than C_3 , formed by opening one of the chelate rings: this phenomenon was found in the trisoxalatocobaltate(III) ion⁽⁸³⁾. On the other hand the α -isomers have C_1 symmetry, so that three Cotton effects are expected for each absorption band. These are observed for Band II of $\alpha(-)\text{-Co}(\text{L-ala})_3$ at 415 m μ , 367 m μ and 330 m μ but only two negative Cotton effects are observed under Band I. It is possible that a transition with a negative Cotton effect at about 525 m μ lies between two positive Cotton effects at about 490 m μ

and 550 mu. It is not uncommon for less components to be observed than are predicted.

The circular dichroism of the $\alpha(+)$, $\alpha(-)$ and $\beta(-)$ -isomers of $\text{Co}(\text{L-ala})_3$ and the $\beta(+)$ -isomer of $\text{Rh}(\text{L-ala})_3$ were measured and are shown in Table 7. These circular dichroisms do not show the high resolution of the measurements in Figures 13 and 14.

Table 7

Circular dichroisms of $\text{M}(\text{amino-acidate})_3$ complexes

Isomer	Band I	Band II
$\alpha(+)]\text{Co}(\text{L-ala})_3$	534 mu +1.97	364 mu -.497
$\alpha(-)-\text{Co}(\text{L-ala})_3$	538 mu -1.56	382 mu +.497
$\beta(-)-\text{Co}(\text{L-ala})_3$	530 mu -2.25	366 mu +.336
$\beta(+)-\text{Rh}(\text{L-ala})_3$	338 mu -1.35	278 mu +.52

If we assume that in the β -isomers the circular dichroism under Band I is principally that of the $E \leftarrow A$ transition⁽¹⁷⁾⁽⁷¹⁾ then the absolute configurations of these isomers can be obtained from the sign of the rotational strength of this transition⁽⁷¹⁾. The $\beta(-)-\text{Co}(\text{L-ala})_3$ and the $\beta(+)-\text{Rh}(\text{L-ala})_3$ complexes have therefore the L configuration. This is consistent with the configuration of the $\beta(-)-\text{Rh}(\text{L-ala})_3$, which was assigned from a solubility observation to the D configuration. If we assume that the larger circular

dichroism band under Band I of $\beta(+)$ -Co(L-ala)₃ is the $E \leftarrow A$ transition then this isomer has the D configuration. The Δ -isomers, which have no symmetry at all cannot be given absolute configurations from a study of their circular dichroism because the only electronic transitions in these complexes are $A \leftarrow A$ transitions. The stereospecificity in these complexes is not very definite and so the absolute configuration of the Δ -isomers cannot be assigned on stereospecific grounds. The only method left is the crystallographic method. This should not be too difficult because the asymmetric carbon atoms of known absolute configuration in the complex can be used as a reference⁽⁸⁴⁾, to which the unknown absolute configuration at the cobalt atom may be compared.

It was unfortunate that the system, which was investigated did not have a genuine homogeneous equilibrium between the isomers and so valid evidence of stereospecificity in the system was not obtained. We have, however, obtained the electronic spectra, the O.R.D. curves and the circular dichroisms of all four isomers of trisL-alaninatocobalt(III). It can be reasonably assumed that the electronic and optical properties of the isomers of other cobalt(amino-acidate)₃ complexes will be very similar. The only difference between various amino-acid complexes is the substituent on the α -carbon in the chelate ring. This should not affect the optical properties. We are therefore in a position to reinvestigate

the two systems, which Lifschitz studied. He claimed to have isolated three isomers of trisL-aspartatocobaltate(III)⁽⁴⁴⁾⁽⁴⁶⁾ and all four isomers of trisL-glutamato-cobaltate(III)⁽⁴⁷⁾.

Aspartic and glutamic acids are dicarboxylic amino-acids and are thus tridentate ligands. The cobalt(amino-acidate)₃³⁻ complexes are, as a result, extremely soluble and so an equilibrium can exist between all the possible isomers. However the large solubility is also a disadvantage as no crystalline salts of these complexes ~~has~~ ^{have} been obtained. The tridentate nature of the ligand increases the possibility of polynuclear complexes. Lifschitz⁽⁴⁴⁾ found evidence for this in the aspartic acid complexes. Dicarboxylic amino-acids can use either of the two carboxylic acid groups to form the chelate rings. However it has been shown⁽⁸⁵⁾ that β-amino-acids form far less stable complexes than α-amino acids. This type of isomerism is therefore improbable.

Any stereospecificity in these cobalt(amino-acidate)₃³⁻ complexes could arise from two sources. The first is the puckering of the chelate ring as in the diamine complexes. This puckering, which is not very large⁽⁵⁷⁾, might be expected to give DB-Co(L-amino-acidate)₃³⁻ greater stability than LB-Co(L-amino-acidate)₃³⁻. The second and the most likely source of stereospecificity is the steric interaction between the substituents on the α-carbon atom in the chelate ring. The interaction in the Δ-isomers would be

much less than in the β -isomers because in the β -isomers three substituent groups are situated in a position to interact with each other while in the α -isomer only two substituent groups can interact. In alanine this group is a methyl group, in aspartic acid it is a $-\text{CH}_2-\text{CO}_2\text{H}$ group and in glutamic acid it is a $-\text{CH}_2-\text{CH}_2-\text{CO}_2\text{H}$ group. An examination of molecular models shows that, in the glutamate complexes, free rotation of the substituent group is impossible. Therefore steric interaction must be large and so some stereospecificity should be evident in this complex.

Lifschitz obtained three α -isomers of trisL-aspartatocobaltate-(III)⁽⁴⁶⁾. Two of these isomers had enantiomorphous O.R.D. curves which are similar to the $\alpha(+)$ and the $\alpha(-)$ -isomers of trisalaninatocobalt(III). The other α -isomer had a completely different O.R.D. curve and was said by Lifschitz to have six-membered chelate rings. Lifschitz has published⁽⁴⁷⁾ the O.R.D. curves of his four isomers of trisL-glutamatocobaltate(III) complexes. They do not appear to be enantiomorphous and are not similar to the curves, which we obtained for the corresponding alaninate complexes. He also claimed that with one method of preparation he obtained the two D isomers and with another method he obtained the two L isomers. We therefore decided to repeat this work to obtain further information about Lifschitz's "isomers". We followed his preparative procedure exactly. It was noticed that

the α -isomers were obtained in far greater amounts than the β -isomers. This confirms the greater stability of the α -isomers and is also in agreement with Lifschitz's observations on the trisL-aspartatocobaltate(III) complexes. The analysis of the compounds agreed reasonably well with Lifschitz's analyses. The visible spectra of the isomers are compared with those of the corresponding isomers of trisL-alaninatocobalt(III) in Table 8.

Table 8

Isomer	Co(L-alaninate) ₃		[Co(L-glutamate) ₃] ³⁻	
	$\lambda(\mu\mu)$	$\frac{\epsilon_{\text{Band II}}}{\epsilon_{\text{Band I}}}$	$\lambda(\mu\mu)$	$\frac{\epsilon_{\text{Band II}}}{\epsilon_{\text{Band I}}}$
α -D	375	1.47	374	1.45
	540		525	
α -L	375	1.59	370	1.59
	540		525	
B-D	375	.85	370	1.3
	516		525	
B-L	375	.77	370	1.93
	516		520	

There is a slight difference in the position of the absorption maxima, λ , between the corresponding isomers, but the main difference is the greater extinction coefficient, ϵ , of Band II compared with Band I of the β -[Co(L-glutamate)₃]³⁻ complexes. In fact the visible

spectra of the $[\text{Co}(\text{L-glutamate})_3]^{3-}$ complexes appeared to be very similar.

We measured the O.R.D. curves of these isomers over a greater range than Lifschitz. Our O.R.D. curves are compared with those of Lifschitz in Figure 19. As in Table 8, we have not given absolute values because the decomposition of the lead and silver salts of the isomers with sodium chloride and sodium sulphate solutions is never complete and also because it was often noticed that the solution deposited cobalt(III) hydroxide on standing and therefore it was impossible to know the concentrations of the solutions.

(Lifschitz⁽⁴⁴⁾ ascribed this decomposition to polynuclear complexes)

The O.R.D. curves of all the isomers are rather similar and are not identical to the O.R.D. curve of any isomer of $\text{Co}(\text{L-alaninate})_3$.

The circular dichroism of the α -D, α -L and the β -D isomers was measured between 600 m μ and 400 m μ . The circular dichroisms are shown in Table 9. There appears to be no similarity between the alaninate (see Table 7) and the glutamate complexes. The glutamate complexes appear to be very similar to one another differing only in the relative sizes of the circular dichroism bands. Two circular dichroism spectra are given for

$\beta(+)\text{-Co}(\text{L-alaninate})_3$. They were obtained from samples prepared by different methods. It was mentioned earlier that it was possible that this isomer might be polynuclear.

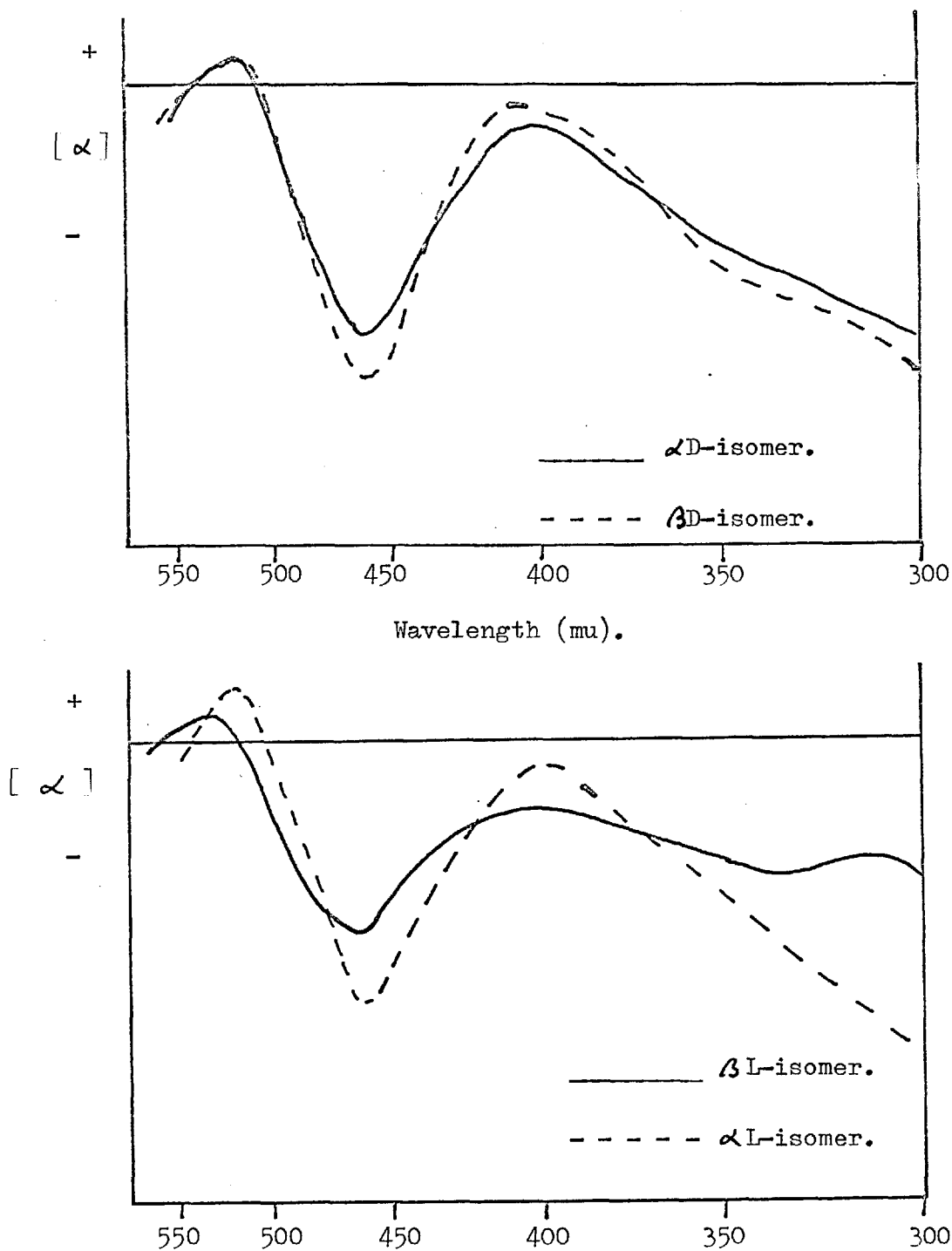


Figure 19. O.R.D. curves of $[\text{Co}(\text{L-glutamate})_3]^{3-}$
(Lifschitz⁽⁴⁷⁾ nomenclature).

Table 9

The Circular Dichroism of Co(amino-acidate)₃ Complexes.

Isomer	$\lambda(\text{m}\mu)$	$\xi_1 - \xi_d$	Relative sizes of bands
α -D Co(L-glutamate) ₃ ³⁻	582		- 1.0
	528		+ 1.51
	472		- 2.2
α -L Co(L-glutamate) ₃ ³	586		- 1.0
	532		+ .84
	476		- 1.34
β -D Co(L-glutamate) ₃ ³	588		- 1.0
	550		+ 1.72
	472		- 1.88
β (+)-Co(L-alaninate) ₃	540	+ .813	
	484	- .335	
	400	+ .112	
β (+)-Co(L-alaninate) ₃	540	+ .855	
	484	- .222	
	400	+ .111	

Polynuclear structures for the trisL-glutamato-cobaltate(III) complexes seem to be the explanation for their differences from the corresponding alaninate complexes. The optical properties suggest that all four of Lifschitz's isomers have the same chirality. The small variations observed in their electronic spectra, O.R.D. curves and circular dichroisms can be explained by geometrical

isomerism or by variations in the polynuclear structure. Mathieu has studied the circular dichroisms of mono-nuclear⁽⁸⁶⁾ and polynuclear⁽⁸⁷⁾ complexes of the type $[\text{Coen}_2\text{XY}]_1^{\text{X}}$ or 2, in which the symmetry at the cobalt atom is the same. He found considerable differences between the mono-nuclear and the binuclear complexes.

The only other $\text{Co}(\text{amino-acidate})_3$ complex that has been studied is the complex with the sulphur-containing amino-acid cysteine. The red isomer of this complex has been shown⁽⁸⁸⁾ to be polymeric. It is very probable that the green isomer⁽⁸⁹⁾ is also polymeric.

Attempts were made to study the equilibrium in the $[\text{Co}(\text{L-glutamate})_3]^{3-}$ system. The sodium salt of the complex was refluxed in aqueous solution with activated charcoal. There was no change in the O.R.D. curve over a short interval. After a longer period the complex decomposed to cobalt(II) compounds. The complex was also treated with an aqueous solution of pyridine but no change occurred. The photochemical effects mentioned by Lifschitz⁽⁴⁷⁾ were not investigated. He observed that the optical rotation changed when the complex was irradiated. This may be a shift in an equilibrium between the isomers or a photoreduction to cobalt(II) compounds.

The only definite conclusions that can be made about the $[\text{Co}(\text{L-glutamate})_3]^{3-}$ complex is that Lifschitz's four isomers are not analogous to the four isomers, which we obtained of the $\text{Co}(\text{L-alaninate})_3$ complex. The shape of the O.R.D. curves and the

sign of the circular dichroism maxima at 530 mμ suggests that all four "isomers" have the D configuration. The "isomers" are very probably polynuclear but this polynuclear structure may involve α , β isomerism. However the α structure seems to be favoured. None of the reaction products appeared to have left-handed helicity. This combined with the failure to observe any change in the properties of the material when boiled for five minutes with active charcoal is good evidence for marked stereospecificity.

PART II

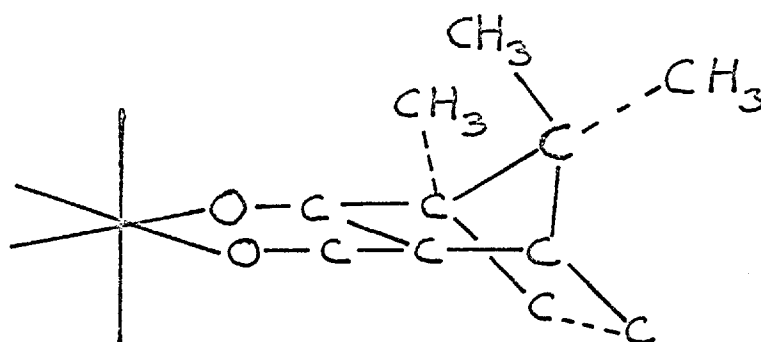
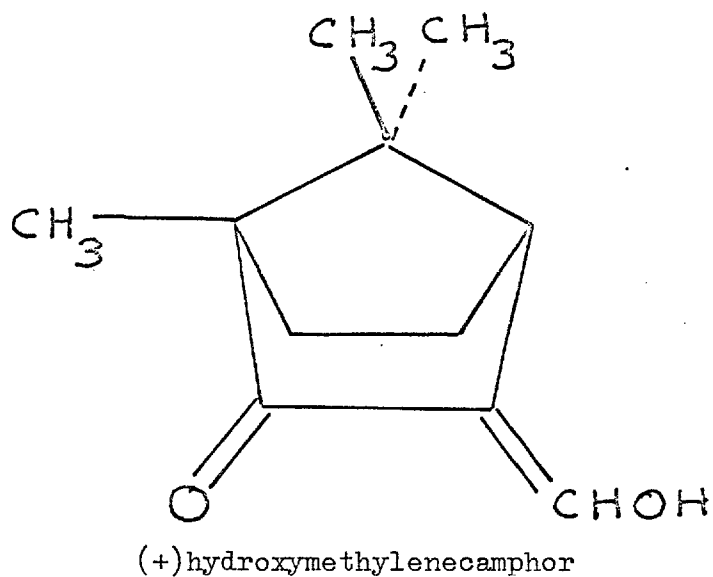
METAL(+FORMYLCAMPHOR)₃ COMPLEXES

Hydroxymethylenecamphor (see Figure 20) is a β -diketone and thus forms stable complexes with metals, which are very similar to the analogous acetylacetonate complexes. However the (+)formylcamphor chelate ring is not symmetrically substituted. The metal(+formylcamphor)₃ complexes should show geometrical isomerism. However this complex is more akin to the Co(propylenediamine)₃ system than the Co(amino-acidate)₃ system and so the isomerism is probably non-existent. The (+)hydroxymethylenecamphor is easily prepared from natural camphor⁽⁹⁰⁾. There will therefore be a total of four possible isomers: D α (+++), L α (+++), D β (+++), and L β (+++).

The chelate ring formed by a metal and a β -diketone is planar⁽⁵⁶⁾. The differences in the stabilities of the diastereoisomers will be the result of steric interaction between the substituents on the chelate ring (see Figure 20). An examination of a molecular model showed that the steric interaction will arise principally from the methyl group on the bridge, which is directed towards the metal atom (see Figure 20).

The metal derivatives of (+)hydroxymethylenecamphor were first mentioned by Claisen⁽⁹⁰⁾ and Lifschitz⁽⁹¹⁾⁽⁹²⁾. Lifschitz later⁽⁹³⁾ reinvestigated the cobalt(III) and the chromium(III) compounds to see if there was any evidence of stereospecificity.

Figure 20



(+)-hydroxymethylenecamphor co-ordinated to a metal with octahedral stereochemistry. A hydrogen atom has been eliminated and therefore the ligand will be referred to as (+)-formylcamphor.

He used the technique of fractional crystallisation. Only one isomer of $\text{Co}(+\text{formylcamphor})_3$ was found but two isomers of $\text{Cr}(+\text{formylcamphor})_3$ were isolated. However one of the latter was quantitatively converted to the other in solution in a day. Therefore there is complete stereospecificity in both cases.

Mason has assigned⁽¹⁷⁾⁽²⁵⁾ the absolute configuration of the $(+)\text{Co}(+\text{formylcamphor})_3$ complex. In the two publications he quotes different spectral and circular dichroism data and suggests that there are two isomers. The assignment of the absolute configuration of this isomer was based on the sign of the $E \leftarrow A$ transition under Band I. This was identified from the polarised absorption spectrum of trisacetylacetonatocobalt(III)⁽⁹⁴⁾. Piper⁽³³⁾ has resolved the trisacetylacetonatocobalt(III) complex and has reported that the $(+)$ complex has a negative Cotton effect at 600 m μ . The O.R.D. curve⁽⁹²⁾ of $(-)\text{Co}(+\text{formylcamphor})_3$ has a positive Cotton effect at about 600 m μ . Mason has stated that the most stable isomer of $\text{Co}(+\text{formylcamphor})_3$ has the D configuration. Therefore we can assign the $(+)\text{Co}(\text{acetylacetonate})_3$ to the L configuration. It should be noted here that there is a disagreement between Lifschitz⁽⁹²⁾ and Mason⁽¹⁷⁾⁽²⁵⁾ as to the sign of the rotation of the most stable isomer of $\text{Co}(+\text{formylcamphor})_3$. This may be the result of a solvent effect, which will be mentioned later.

It was decided to re-examine the stereospecificity of these

complexes with modern experimental techniques. The cobalt(III) complex was prepared by the method of Lifschitz⁽⁹¹⁾. The ligroin-soluble fraction of the reaction product was chromatographed on an alumina column. The material passed through in one band leaving a small fraction of a green material at the top of the column. This was identified as the polynuclear compound mentioned by Lifschitz. A small fraction of the eluted material was further chromatographed on a 90 cm. column of D-lactose monohydrate. However this optically active adsorbent did not produce any fractionation. We therefore came to the same conclusion as Lifschitz. There was a considerable solubility difference between the diastereoisomers of the chromium(III) complex. If the diastereoisomers of the cobalt(III) complex have the same solubility differences - a not unreasonable assumption, then the chromatographic techniques would have separated them if both isomers had been present.

The equilibration of the $(-)\text{Co}(+\text{formylcamphor})_3$ isomer was studied. The isomer was refluxed in methanol with activated charcoal for ten minutes but no change in the optical activity was observed. After three hours boiling the optical activity was considerably reduced but the shape of the O.R.D. curve remained substantially unaltered. After twenty-four hours refluxing, the isomer had completely decomposed to a mixture of cobalt(II) compounds and the polymeric cobalt(III) compound. The equilibration of cobalt(III) compounds⁽⁷³⁾⁽⁹⁵⁾ is usually complete in five minutes.

Trisacetylacetonatocobalt(III) has been shown to be optically unstable⁽⁹⁶⁾. The (-)tris(+)formylcamphorcobalt(III) complex must therefore have sufficient lability to allow equilibration if this was thermodynamically favourable. The equilibration results suggest that one isomer is favoured to the exclusion of all others.

The trisacetylacetonatorhodium(III) complex has been prepared⁽⁹⁷⁾ and resolved⁽⁹⁶⁾. Unfortunately, only the magnitude of the rotation of the resolved complex was reported and not the sign. (+)hydroxymethylenecamphor reacts with rhodium(III) chloride in a similar manner. Three compounds were isolated. One of these was separated from the other two because of its insolubility in ligroin. The ligroin-soluble material was separated by chromatography on alumina into two fractions. The first fraction was recrystallised three times but the optical activity did not change. This compound, which is therefore optically pure, analysed as (-)tris(+)formylcamphor-rhodium(III). The second fraction had a much smaller Cotton effect. Recrystallisation from several solvents showed that it contained some of the former fraction. The separation of this mixture is not yet complete but the electronic spectrum and the infra-red spectrum of the mixture are identical with that of the optically pure compound. The O.R.D. curve of the mixture appears to be the inverse of the (-)Rh(+formylcamphor)₃ isomer therefore we believe that the mixture contains the (+)Rh(+formylcamphor)₃ isomer. The ligroin-insoluble material has not been fully investigated but its

electronic and infra-red spectrum shows that it is different from the other two compounds. The infra-red spectrum suggests that it is a hydrate.

The (-)-isomer and the mixture were refluxed in methanol with activated charcoal for nine hours but neither showed any change in optical activity. Rhodium(III) compounds are much more kinetically inert than cobalt(III) compounds. This probably explains why absolute stereospecificity has not been observed. The isomers were formed in a ratio which was controlled by the kinetics of the reaction but because of the kinetic inertness of both of the isomers, the thermodynamic equilibrium has not been attained.

The optical activity of the charge transfer band of these complexes masks the Cotton effects, which are associated with the d-d transitions. The absolute configuration of the (-)-isomer cannot therefore be given. The O.R.D. curves of the (-)Rh(+formylcamphor)₃ and the mixture are given in Figure 21.

The infra-red spectra of the (-)Rh(+formylcamphor)₃ and the (-)Co(+formylcamphor)₃ isomers are identical but they differ from the spectra of the acetylacetonate complexes as is shown in Table 10. This difference is interesting because of the various assignments given to the bands of the trisacetylacetonate complexes⁽⁹⁸⁾⁽⁹⁹⁾⁽¹⁰⁰⁾. The principal differences in the spectra are the shift of the bands of the trisacetylacetonate complexes at ca. 1580 cm⁻¹ and ca. 1515 cm⁻¹.

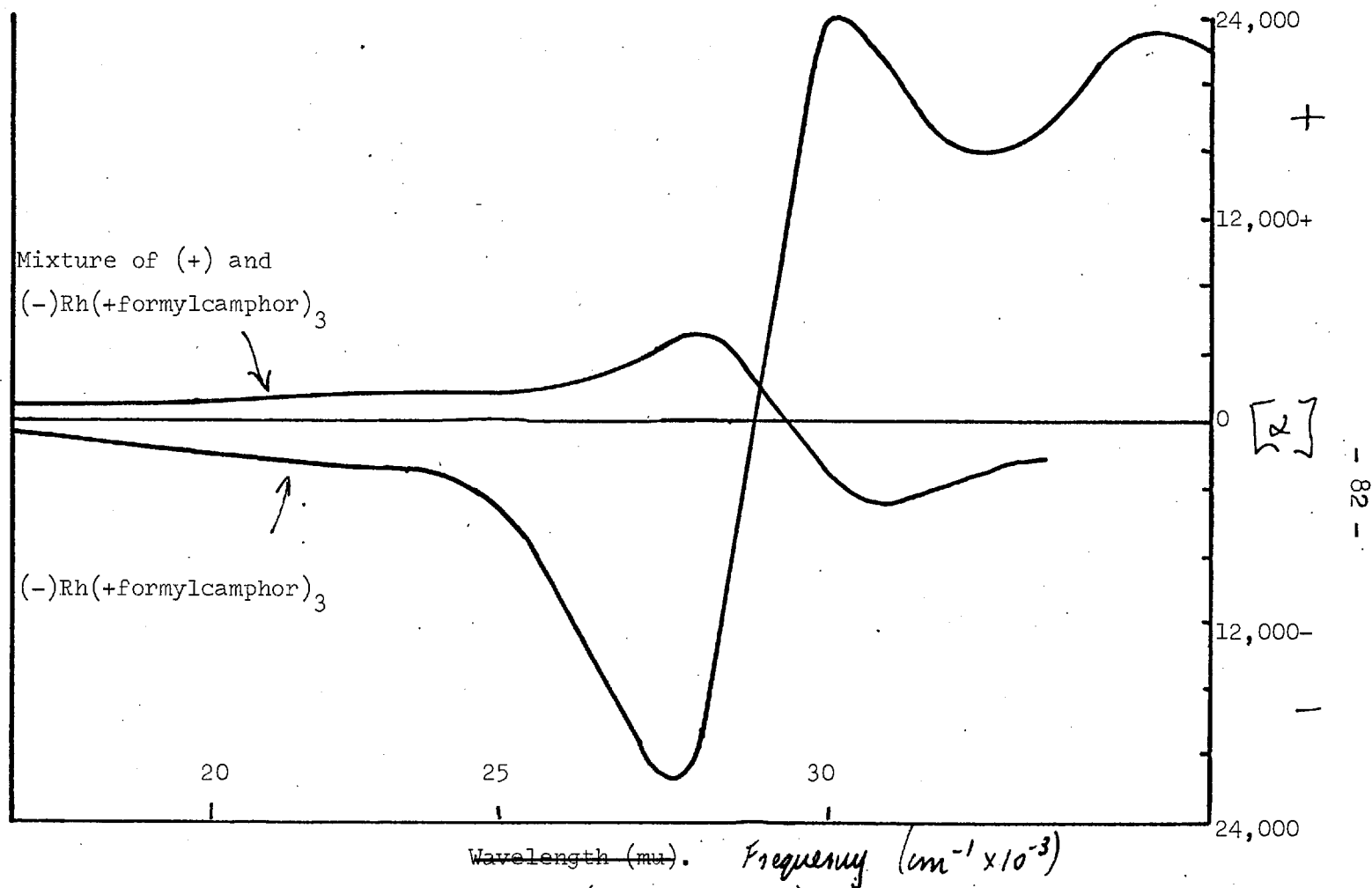


Figure 21.

O.R.D. curves of $\text{Rh}(+\text{formylcamphor})_3$.

Table 10

Infra-red spectra of $M(\text{acetylacetonate})_3$ and $M(+\text{formylcamphor})_3$
complexes where M is cobalt or rhodium.

$M(\text{acetylacetonate})_3$		$M(+\text{formylcamphor})_3$	
cm^{-1}	Intensity	cm^{-1}	Intensity
2400	vs.	2400	vs.
1580	s.	1620	s.
1515	s.		
1460	s.	1460	s.
1380	s.	1380	ms.
		1320	ms.
1280	ms.	1280	ms.
		1215	w.
1210	m.		
		1140	w.
		1155	m.
		1110	m.
		1075	m.
		1050	w.
1020	m.	975	w.
935	m.	915	w.
790	w.	795	w.
775	m.	750	m.
720	w.	725	m.
710	w.		

The spectra were measured as nujol mulls.

In the trisformylcamphor complexes the former seems to shift to higher energy and the latter to lower energy. The main structural difference between these two complexes is the inclusion of a C-C bond of the chelate ring in a five-membered ring in the formylcamphor complexes. It might be expected that the stretching frequency of this bond would be decreased in the trisformylcamphor complexes and that a possible reduction in the delocalisation of the chelate ring would increase the frequency of the carbonyl vibrations. We therefore feel that Nakamoto's assignments are wrong. Three recent assignments of principal bands are given in Table 11.

Table 11

Assignments of absorption bands in the infra-red spectra of acetylacetonate complexes.

Band cm ⁻¹	Lecomte (98)	Mecke (99)	Nakamoto (100)
1630 - 1567	a. CO str.	CO str.	a. C-C str.
1560 - 1517	C-C str.	C-C str.	s. CO str.
1486 - 1431	CH ₃ def.	CO str.	s. CO str.+CH bend
1429 - 1357	sym. CO str.	CH ₃ def.	CH ₃ def.

PART III A SOLVENT EFFECT OF (-)TRIS(+)FORMYLCAMPHORCOBALT(III)

A paper⁽¹⁰¹⁾ has been published describing the variation of the nuclear magnetic resonance of the cobalt⁵⁹ nucleus in trisacetyl-acetonatocobalt(III) in different solvents. The authors could not attribute the noticeable chemical shift to any property of the solvent. We examined the variation of the d-d electronic transition at 596 mμ in different solvents. The variation in the position of the absorption maximum was about 2 mμ, while the variation in the extinction coefficient of this band was about five per cent. This was not large enough for accurate measurements. It was therefore decided to study the effect of the solvents on the optical activity of (-)Co(+formylcamphor)₃, which is assumed to be electronically analogous to the acetylacetonate complex. The d-d transition in this complex is at 608 mμ. The O.R.D. curve was measured in this region with six different solvents. The specific rotation at 500 mμ was taken as the best measure of the solvent effect. $[\alpha]_{500}$ showed a twenty per cent variation over the six solvents.

Table 12

The solvent effect of Co(+formylcamphor)₃

Solvent	Dielectric Constant	$[\alpha]_{500}$
Carbon tetrachloride	2.24	4800°
Benzene	2.27	4930°
Chloroform	5.05	4650°
Chlorobenzene	5.94	4750°
Acetone	21.4	4250°
Methanol	33.1	3760°

The variation in the optical activity is just another manifestation of the phenomenon, which produced the variation in the extinction coefficient. The rotational strength, R , of an electronic transition is proportional to the electric transition moment and therefore to the square root of the dipole strength of that transition⁽¹⁷⁾. The electric transition moment is a measure of the allowedness of the transition. While the magnetic transition moment will be approximately constant⁽¹⁷⁾, the electric transition moment will vary as the "mixing in"⁽¹⁰²⁾ of higher energy levels varies. The interaction of the solute and the solvent will control this "mixing in".

The effect of the solvent on the electronic spectrum and the optical activity of transition-metal complexes has been observed in many instances. The effect has been attributed to two causes: ion-pairing and the direct action of the solvent on the metal chromophore. The effect of ion-pairing on the optical activity of complex ions has been studied very fully⁽²⁷⁾⁽⁷³⁾⁽¹⁰³⁾⁽¹⁰⁴⁾. The solvent effects, which are caused by the direct action of the solvent on the metal atom, are illustrated by bisacetylacetonatocopper(II)⁽¹⁰⁵⁾, bisacetylacetonatooxovanadium(IV)⁽¹⁰⁶⁾ and bis(+)formylcamphor-copper(II)⁽¹⁰⁷⁾. However the solvent effects, which we have observed, cannot be explained by the above mechanisms because $\text{Co}(+\text{formylcamphor})_3$ is a neutral molecule and the metal atom is

shielded from direct interaction with the solvent by the ligand molecules. The solvent effect is therefore a result of the interaction of the solvent and the ligands. Lifschitz⁽⁹²⁾ has in fact observed solvent effects with (+)hydroxymethylenecamphor.

The electric field seen at one molecule arising from the dipoles of its neighbours is equal to $\frac{\epsilon+2}{3}$, where ϵ is the dielectric constant of the solvent. Figure 22 shows $\frac{\epsilon+2}{3}$ plotted against $[\alpha]_{500}$ for the six solvents. It is interesting to note that the term $\frac{n^2+2}{3}$, (where n is the refractive index of the solvent), is included in the constant K in the quantum mechanical expression for optical rotatory power⁽¹⁰⁸⁾. Kauzman, Walter and Eyring⁽¹⁰⁸⁾ have shown that this relationship explains the effect of thirty-six solvents on the optical activity of pinane⁽¹⁰⁹⁾. The optical activity of Co(+formylcamphor)₃ is greater in the less polar solvents. It was observed that the extinction coefficients of the d-d band in Co(acetylacetonate)₃ were also higher in the less polar solvents. Lifschitz⁽⁴⁵⁾ measured the O.R.D. curves of the α -Co(L-alaninate)₃ isomers in water and in 50% sulphuric acid. He noticed a solvent effect but in this case the solute was almost certainly protonated. He also observed that the optical activity of (+)Cr(+formylcamphor)₃ was affected by a change in the solvent used. However as he had discovered that an equilibrium exists between this isomer and another isomer of Cr(+formylcamphor)₃, the solvent may just be changing the position of this equilibrium.

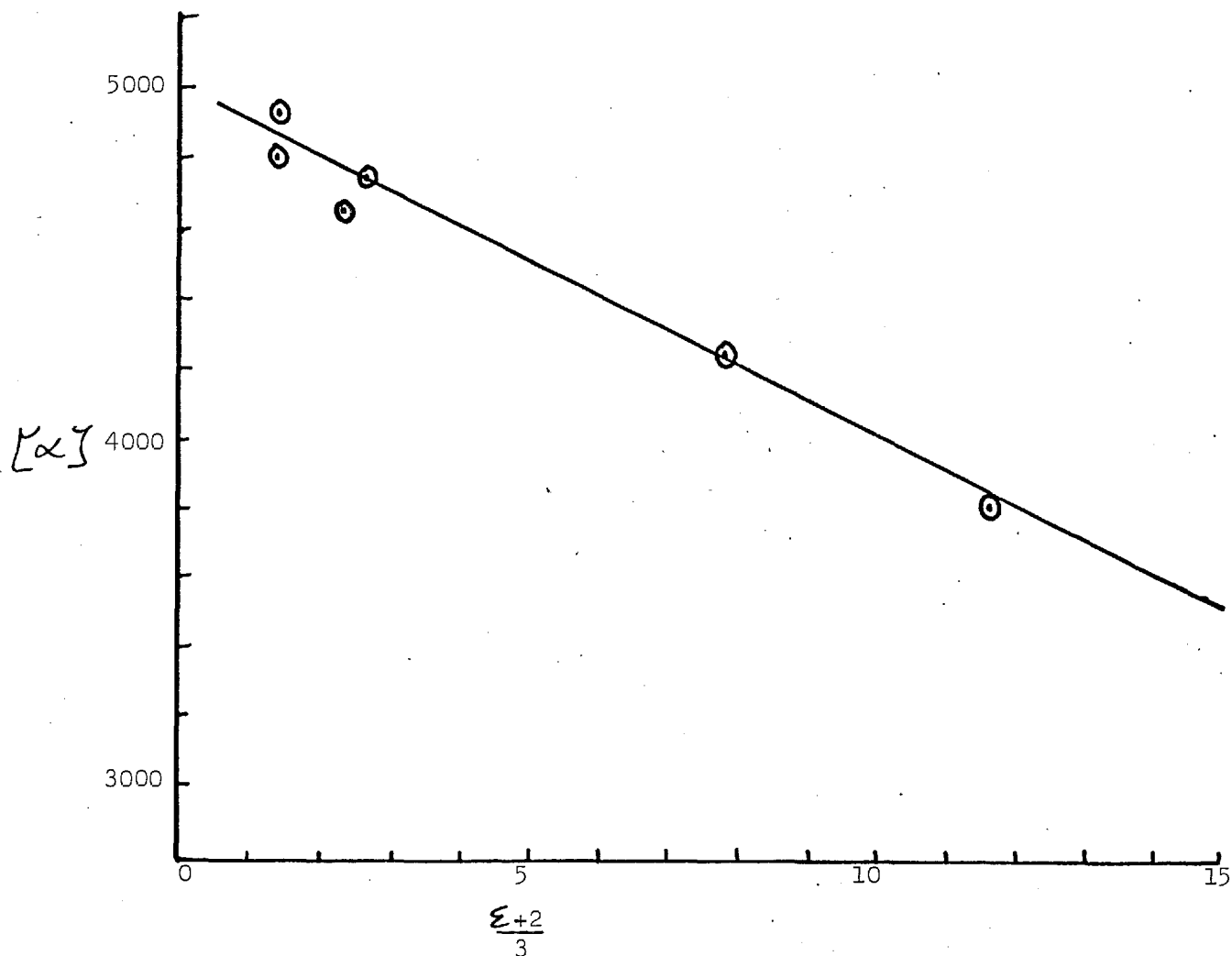


Figure 22. The specific rotation of $(-)\text{Co}(+\text{formylcamphor})_3$ plotted against the term $\frac{\epsilon+2}{3}$, where ϵ is the Dielectric constant.

The solvent effect, which we have described, cannot be attributed to either of these two causes and therefore it must be the first definite case of the effect of the solvent on the d-d transitions of a metal complex which is purely dipolar in nature. These results are not inconsistent with the chemical shift studies⁽¹⁰¹⁾. Richards and his co-workers showed that, for a number of cobalt(III) complexes, the chemical shifts of the cobalt⁵⁹ were dependent on the separation of the ground state and the first excited state. This means that the solvent effect that they observed was associated with a change in the position of the d-d band. If this effect was considerable then there would be a change in the specific rotation at 500 mμ even if there was no change in the allowedness of the transition. From the straight line in Figure 22 it can be concluded that the major influence of the solvent on $(-)\text{Co}(+\text{formylcamphor})_3$ is on the allowedness of the electronic transition. The transitions are more allowed in non-polar solvents than in polar solvents.

CHAPTER IV

THE VICINAL EFFECT

This chapter is divided into two parts. The first part deals with the nature of the vicinal effect in transition-metal complexes and its use as a means of comparing the configurations of organic compounds. The second part of the chapter demonstrates how asymmetric ligands can be used to study the electronic transitions of non-resolvable metal complexes.

PART I

ACIDOPENTAMINE- AND ACIDOTETRAMMINECOBALT(III) COMPLEXES.

The Cotton effects, which are observed in organic compounds (17)(110), are associated with the electronic transitions of chromophores, which are not dissymmetric. Examples are the $n-\pi$ transitions of the carbonyl and nitro groups and the $\pi-\pi$ transitions of the C=C group. These transitions are simultaneously electric and magnetic-dipole allowed but the rotatory power is provided by an asymmetric perturbation from a nearby asymmetric carbon atom. This is the vicinal effect which was first discussed by Tschugaeff⁽¹¹¹⁾, Lifschitz⁽⁹²⁾ and Kuhn⁽¹¹²⁾. Condon, Altar and Eyring⁽¹¹³⁾ have used this vicinal effect in their coupled harmonic-oscillator theory of optical activity. The octant rule⁽³⁶⁾ for dissymmetric ketones is interpreted by the direction of this vicinal action on

the carbonyl chromophore⁽¹¹⁴⁾. Djerassi⁽¹¹⁵⁾ has shown that the size of the rotatory power of this transition falls away sharply as the distance between the asymmetric group and the chromophore increases.

Unfortunately the theories of the optical activity of transition-metal complexes have concentrated on those complexes, in which the chromophore is dissymmetric. The vicinal effect, that is the effect of an optically active ligand on a symmetrically co-ordinated metal atom, has been neglected. The recent theory of Liehr⁽¹¹⁶⁾, which deals with the optical activity of dihedral molecules, states that the rotational strength of the electronic transitions of the metal is proportional to the distortion of the metal orbitals, which is caused by chelation. There is much evidence to show that the optical activity of metal chelates increases with the number of chelate rings⁽¹¹⁷⁾ but some workers⁽¹¹⁸⁾⁽¹¹⁹⁾ have assumed from this that chelation is a condition for the observation of optical activity and have dismissed the vicinal effect of optically active ligands as being negligible. This is essentially a revival of an old controversy concerning the geometrical structure of four co-ordinated copper(II) and nickel(II) complexes, which is very well discussed by Martell and Calvin⁽¹²⁰⁾. The O.R.D. curves of many complexes of copper(II) and nickel(II) with diamines, amino-acids, β -diketones and Schiff bases showed strong Cotton effects in the

visible region of the electronic spectrum⁽⁴⁴⁾⁽⁹²⁾⁽¹⁰⁷⁾⁽¹²¹⁾. Several authors, but principally Pfeiffer⁽¹²²⁾, argued that this was evidence for non-planar structures for these complexes. The magnetism of Lifschitz's salts⁽⁵⁰⁾⁽⁶⁴⁾⁽¹²³⁾ at that time interpreted by the valence bond theory suggested that the yellow isomers were planar and that the blue isomers were tetrahedral. However the yellow isomer had a stronger Cotton effect in the visible region than the blue isomer. Lifschitz⁽⁶⁴⁾ therefore concluded that the Cotton effects arose from a molecular dissymmetry rather than from the dissymmetry of the metal atom. Larsen and Olsen in a recent paper⁽¹¹⁸⁾ state that the Cotton effects in copper(II) lactate complexes can only be explained by a molecular dissymmetry produced by a puckering of the chelate rings similar to that in diamines. In contrast, Wentworth and Piper⁽¹²⁴⁾, who studied the electronic spectra and the circular dichroisms of diacidobis(-)propylenediamine-cobalt(III) complexes, state that the electronic spectrum is not affected by the presence or absence of a centre of symmetry but that the circular dichroism is affected by a vicinal electric moment from the axial ligands.

The only genuine study of the vicinal effect must be done with complexes, which have no chelate rings. This will eliminate many of the arguments, which have been used against the vicinal effect. Larsen and Olsen⁽¹¹⁸⁾ claimed that in copper(II) (+)- α -methylbutyrate, tetrakis(+)-2-aminobutanecopper(II), trans-di(+)- α -methyl-

butyrato tetramminecobalt(III) and (+)- α -methylbutyrato pentamminecobalt(III) complexes no Cotton effects were observed in the region of their d-d transitions. However Kirschner⁽¹²⁵⁾ has observed a marked Cotton effect with a (+)-tartrato pentamminecobalt(III) ion in the region of the absorption band at 500 m μ . Larsen and Olsen appear to have chosen unsuitable complexes for a study of the vicinal effect. The copper(II) (+)- α -methylbutyrate will ionise in aqueous solution. Kirschner has demonstrated that optically active anions have no vicinal action on cations. Bjerrum⁽¹²⁶⁾ showed that the $[\text{Cu}(\text{n-butylamine})_4]^{2+}$ complex was thermodynamically unstable in aqueous solution and that it would only be present in appreciable amounts when a large excess of the amine was present. No study has been made of the rate of aquation of trans-diacetato-bisethylenediaminecobalt(III) ions but Mathieu⁽¹²⁷⁾ measured the half-life of the trans- $[\text{Co}(\text{p}_2\text{Cl}_2)]^+$ ion and obtained a value of 3.57 hours. The acetato pentamminecobalt(III) complexes aquate readily in aqueous solution⁽¹²⁸⁾. Larsen and Olsen do not give much experimental detail but they do not appear to have realised the instability of the complexes they chose to investigate.

Several new acidopentamminecobalt(III) complexes were made and studied to confirm Kirschner's results and to see if the sign of this Cotton effect at 500 m μ could be used to compare the configuration of organic acids. Acidopentamminecobalt(III) complexes

were prepared with (+)lactate, (-)malate and acetate as the ligand. The acetato-(129) and the lactatopentamminecobalt(III)(128) complexes have been prepared before. The preparation involved the addition of two equivalents of the acid to one equivalent of $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{NO}_3$ dissolved in water. The solutions were evaporated to low volume at a temperature not exceeding 45° . If the solutions with lactic acid and malic acid were heated above that temperature, ammonia was evolved and the complex decomposed. With the exception of the (-)malato-complex the complexes were obtained as crystalline solids and were characterised by their analyses and electronic spectra. The (-)malato-complex was very deliquescent and was therefore characterised through its electronic spectrum. The O.R.D. curves of the two complexes with the asymmetric ligands are given in Figure 23. The Cotton effects confirm that the conjugate base of these acids is co-ordinated to the metal and that aquation is not complete. The rate of aquation of several C-substituted acetatopentamminecobalt(III) complexes was shown(128) to be related to the base strength of the co-ordinated ligand. The relatively small amplitudes of the Cotton effects suggest that these complexes are unstable. However the amplitude is large enough to show that the vicinal effect is not negligible. A very recent paper(130) reports the O.R.D. curves and circular dichroisms of amino-acidatopentamminecobalt(III) complexes.

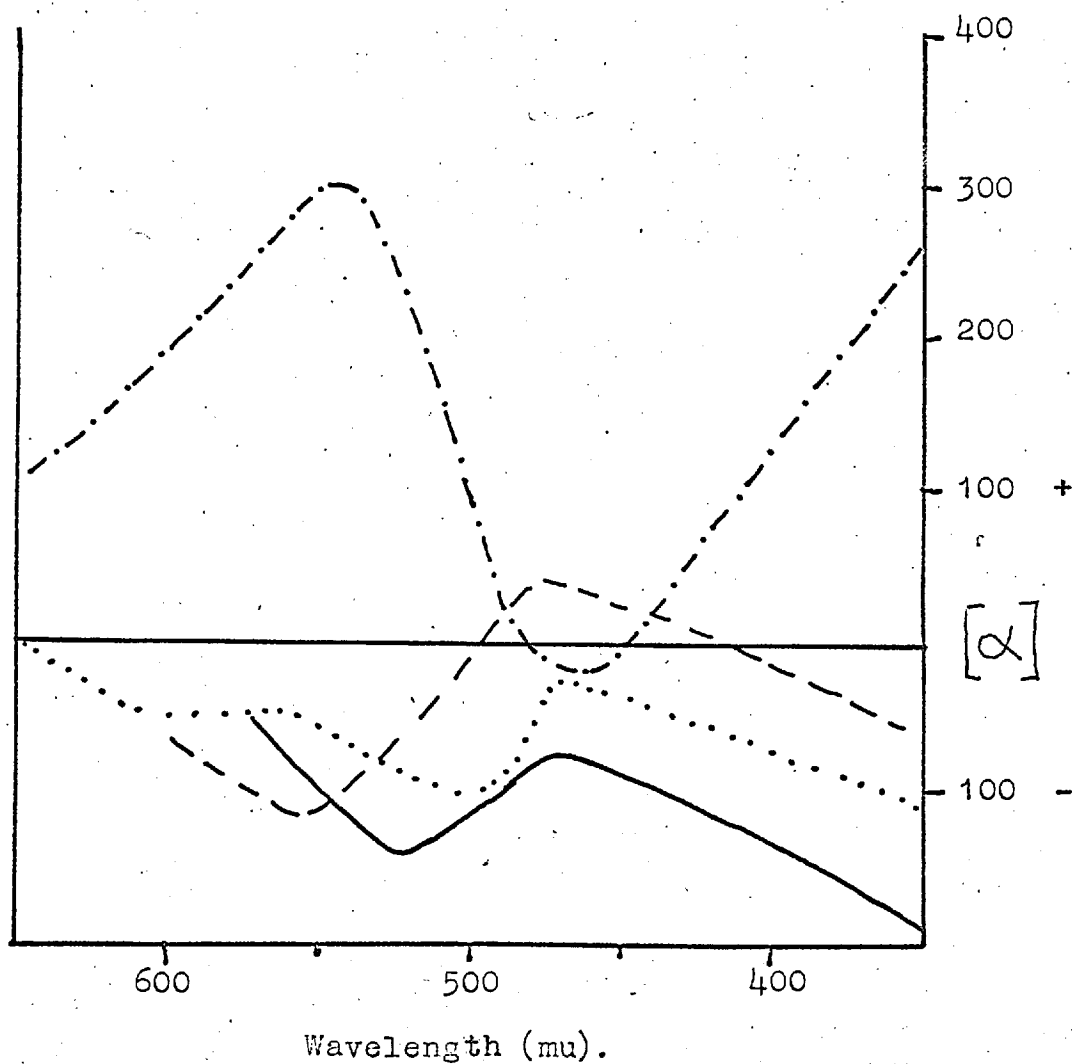


Figure 23. O.R.D. curves of acidopentamminecobalt(III) complexes.

- $[\text{Co}(\text{NH}_3)_5\text{L+lactate}]^{2+}$ (this work)
- $[\text{Co}(\text{NH}_3)_5\text{L+alaninate}]^{3+}$ (130)
- - - - $[\text{Co}(\text{NH}_3)_5\text{L-malate}]^+$ (this work)
- . . . - $[\text{Co}(\text{NH}_3)_5\text{D+tartrate}]^+$ (125)

In this work earlier attempts to prepare these compounds were unsuccessful. The compounds appeared to be unstable, decomposing to tetrammine complexes. The O.R.D. of the L-alaninato complex is included in Figure 23. The very small circular dichroism of this compound reported by the Japanese workers shows two peaks under Band 1 of the electronic spectrum. This is consistent with the C_{4v} symmetry of the complex ion. The variations in the shape of the O.R.D. curves can be explained by the differences in the charge of the complex cation, which will affect the degree of ion-pairing. Ion-pairing is known to affect the optical activity of a complex ion to a considerable extent⁽²⁷⁾⁽⁷³⁾⁽¹⁰³⁾⁽¹⁰⁴⁾. The visible spectra of these acidopentamminecobalt(III) ions are given in Table 13. It can be seen from this table that the complexes are all of the same type.

Table 13

The electronic spectra of acidopentamminecobalt(III) ions.

Ion	Band I		Band II		Ref.
	$\lambda(\mu)$	ϵ	$\lambda(\mu)$	ϵ	
$[\text{Co}(\text{NH}_3)_5\text{acetate}]^{2+}$	504	66	352	50	131
$[\text{Co}(\text{NH}_3)_5(+)\text{lactate}]^{2+}$	501	55	350	47	a
$[\text{Co}(\text{NH}_3)_5(-)\text{malate}]^{2+}$	501	-	349	-	a
$[\text{Co}(\text{NH}_3)_5(+)\text{tartrate}]^{2+}$	505	-	-	-	125
$[\text{Co}(\text{NH}_3)_5(+)\text{alanine}]^{3+}$	500	68	350	54	130

a This work.

Table 14

A comparison of the configurations of organic acids by the Cotton effects of their acidopentamminecobalt(III) complexes.

Acid	Sign of Band I Cotton effect	Absolute configuration from chemical correlation
(+)tartaric acid	+	D
(+)lactic acid	-	L
(-)malic acid	-	L
(+)alanine	-	L

The chemical correlations are well reviewed in references 1 and 135.

The signs of the long-wavelength Cotton effects of the four optically active complexes are given in Table 14. The relative configurations of these acids are known from chemical correlations. The absolute configuration of (+)tartaric acid is known from Bijvoet's⁽¹⁸⁾ crystallographic study. If it is assumed that acids with the same absolute configuration induce Cotton effects at the metal chromophore with the same sign, then it can be seen from Table 14 that the physical method of comparing configurations is in agreement with the chemical method. Similar physical methods have been used in the past to compare the configurations of organic acids and they have proved to be reliable. Pfeiffer and Karrer both used copper(II) complexes to compare the configurations of α -amino-acids⁽¹³⁶⁾. Pfeiffer found that this metal was not very suitable for the comparison of α -amino-acids with α -hydroxy-acids⁽¹³⁷⁾. Mathieu⁽¹³⁸⁾ has used $[\text{Co}(\text{diamine})_2 \text{ amino-acidate}]^{2+}$ ions and Dunlop and Gillard⁽¹³⁹⁾ have used $[\text{Co}(\text{NH}_3)_4 \text{ amino-acidate}]^{2+}$ ions to compare the configurations of α -amino-acids. Cobalt(III) complexes are very suitable for the comparison of configurations because their visible spectra are well understood. These very satisfactory results with acids of known absolute configuration suggest that acidopentammine-cobalt(III) complexes could be used to compare the configuration of acids, which cannot easily be correlated with the standard compounds by chemical methods.

Complexes of the type $[\text{Co}(\text{NH}_3)_4(\text{amino-acidate})]^{2+}$ are known⁽¹⁴⁰⁾ and Shimura⁽¹⁴¹⁾ measured the O.R.D. curve of the L-leucinato-complex. In this work, the complexes with D-alanine and L-histidine and L-leucine were prepared. The circular dichroisms and the electronic absorption spectra are given in Table 15. The signs of the Cotton effects are in agreement with the relative configurations of the amino-acids.

Table 15
The Cotton effects of acidotetramminecobalt(III) ions.

Complex ion	Electronic absorption		Circular dichroism	
	$\lambda(\text{m}\mu)$	ϵ	$\lambda(\text{m}\mu)$	$\epsilon_1 - \epsilon_2$
$[\text{Co}(\text{NH}_3)_4\text{D-ala}]^{2+}$ (a)	487	60	515	-.1
	347	66	460	+.39
			345	+.08
$[\text{Co}(\text{NH}_3)_4\text{L-leu}]^{2+}$ (b)	493	85	512	+.12
	348	88	463	-.32
			347	-.09
$[\text{Co}(\text{NH}_3)_4\text{L-hist}]^{2+}$	492	74	576	+.10
	340	217	490	-.39
			not measured	
$[\text{Co}(\text{NH}_3)_4\text{D-tart}]^+$	515	66	525	+.20
	355	65	415	-.08

Abbreviations: D-ala. D-alaninate.
 L-leu. L-leucinate.
 L-hist. L-histidinate.
 D-tart. D-tartrate.

(a) spectrum identical with that of reference 140;

(b) spectrum identical with that of reference 141.

The circular dichroism of the L-leucinato-complex is in agreement with the analysed O.R.D. curves of the same complex⁽¹⁴¹⁾. The configuration of D-tartaric acid cannot be compared with those of the amino-acids from the results in Table 15 because the tartrato-complexes have a different symmetry and therefore the splitting of the energy levels in the cobalt atom in this complex is not equivalent to the splitting in the amino-acido-complexes. This is the first time that the circular dichroism of cobalt(III) complexes with only one chelate ring has been measured. There have been previous O.R.D. studies of cobalt(III) complexes with a single diamino chelate ring⁽¹⁴²⁾. They are all a confirmation of the vicinal effect. The size of the circular dichroism bands is very interesting. In the $[\text{Co}(\text{NH}_3)_4\text{amino-acidate}]^{2+}$ ions, in which the environment of the metal atom can be said to have C_S symmetry (all transitions are non-degenerate) the maximum circular dichroism is about 0.4 for Band I and 0.1 for Band II. This shows that even although all transitions are magnetic-dipole allowed, the selection rules for O_h symmetry still control the relative rotational strengths of the transitions in a complex, whose symmetry is far removed from O_h . Mathieu has measured the circular dichroism of the electronically similar $[\text{Coen}_2\text{amino-acidate}]^{2+}$ ions⁽¹³⁸⁾. He found that the size of the circular dichroism under Band I is 1.86 for the L-alaninato-complex. This reflects the difference in the rotational strength of the longest wavelength absorption band between a complex, which derives

its rotational strength from the asymmetry of the chromophore and a complex, which derives its strength from a vicinal effect.

An examination of the circular dichroisms of the compounds, which we have studied, shows that some generalisations can be made about the magnitude of the phenomenon in various complexes. It appears that the Cotton effect in metal complexes is related to the number of chelate rings in the molecule. Compounds with one chelate ring have a circular dichroism about 0.4, those with two chelate rings about 0.9 and those with three chelate rings about 1.8. Gillard⁽¹¹⁷⁾ has illustrated this point further. The circular dichroisms of $[\text{Coen}_3]^{3+}$, $[\text{Co}(+pn)_3]^{3+}$ and $\text{Co}(\text{L-alaninate})_3$ are all of the same magnitude. The vicinal effect does not appear to have any significance in these complexes. In tetragonal complexes and in complexes with only one chelate ring, the molecule will be dissymmetric if only one optical isomer of the asymmetric bidentate ligand is present, whether the chelate ring is planar or puckered. In such cases it is difficult to say whether the Cotton effects are a result of this molecular dissymmetry or just of a vicinal effect. The acidopentammine complexes, which showed Cotton effects associated with the d-d transitions, are also dissymmetric. Therefore vicinal action in transition-metal complexes can only be definitely proved by studying the relationship between the Cotton effect of the chromophore and the distance between that chromophore

and the asymmetric centre.

Unfortunately the Kuhn dissymmetry factor, g ,⁽¹⁵⁾ cannot be used as a measure of dissymmetry in transition-metal complexes, because all the Cotton effects in dissymmetric complexes are associated with absorption bands, which are produced by two or more electronic transitions. The Cotton effects associated with these transitions are of opposite sign and because of their proximity are mutually cancelled to an extent, which depends on the difference of energy between them. The size of the Cotton effects are also affected by the borrowing of transition moment from transitions of higher energy. The Kuhn dissymmetry factor, therefore, can only be used as a qualitative guide to the magnetic dipole allowedness of the electronic transitions in metal complexes⁽¹⁴⁾⁽¹⁷⁾.

PART II

TETRAGONAL COBALT(III) AND RHODIUM(III) COMPLEXES

The use of the Cotton effects of transition metal complexes to study the structure of the complex and the absolute configuration of both the complex and any asymmetric ligands is now well established. However, optical activity has played a very small part in the study of the electronic spectra of these complexes. The electronic transitions of metal complexes with the spin-free d^3 or the spin-paired d^6 ground state become polarised when the symmetry of the complex is reduced. The dependence of the allowedness of a transition on the direction of the incident light has been used considerably but its successful application demands a knowledge of the crystal structure of the metal complex. The magnetic-dipole allowed transitions are also polarised but the polarised circular dichroisms of asymmetric compounds has been studied in very few cases⁽²⁵⁾. It is now fairly certain that, when a $T \leftarrow A$ transition is split into $E \leftarrow A$ and $A \leftarrow A$ transitions, the $E \leftarrow A$ transition will have the larger rotational strength. Several $E \leftarrow A$ transitions have been identified in this way⁽²⁵⁾⁽³⁴⁾⁽⁷²⁾.

It was decided to use magnetic-dipole selection rules to study the visible spectrum of a well-known class of co-ordination compounds - the trans-dichlorotetraamminecobalt(III) complexes. The trans-dichlorobisdiaminecobalt(III) complexes have a very similar

electronic spectrum to the trans-[Co(NH₃)₄Cl₂]⁺ complexes⁽¹³¹⁾. The splittings of the energy levels in both complexes must be very similar and they can be treated as if they belonged to the D_{4h} point group (see Table 3). Moffitt and Ballhausen⁽¹⁴³⁾ have measured the absorption of polarised light by orientated crystals of trans-[Co(en₂Cl₂)]ClO₄. These complexes have a centre of symmetry and Piper⁽¹²⁴⁾ has shown that the intensity of the visible spectrum arises solely from vibronic coupling. Moffitt and Ballhausen interpreted their results in terms of vibronic coupling. They confidently assigned the absorption band at 625 mμ. to the ${}^1E_g \longleftrightarrow {}^1A_{1g}$ transition but the band at 424 mμ. could not be definitely assigned. From the results of the polarised absorption spectrum, it could be either the ${}^1A_{2g} \longleftrightarrow {}^1A_{1g}$ or the ${}^1B_{2g} \longleftrightarrow {}^1A_{1g}$ transition.

We prepared the trans-[Co(-pn)₂Cl₂]⁺ complex and measured its circular dichroism. The electronic spectrum and the circular dichroism of this ion are given in Table 16. The magnetic-dipole selection rules for the D_{4h} group are given in Table 3. Only the ${}^1B_{2g} \longleftrightarrow {}^1A_{1g}$ transition is magnetic-dipole forbidden. This complex is planar and thus non-resolvable but the rotational strengths of the transitions have come from the vicinal effects of the asymmetric ligands. The ${}^1E_g \longleftrightarrow {}^1A_g$ transition has been assigned⁽¹⁴³⁾ and the size of the circular dichroism band confirmed this assignment. The band at 424 mμ., which does not give a Cotton effect, was assigned by us⁽¹⁴⁵⁾ to the ${}^1B_{2g} \longleftrightarrow {}^1A_{1g}$ transitions. The band at 520 mμ. was

Table 16

Electronic spectra of trans-dichlorotetramminecobalt(III) compounds

a	Old assign- ment (D_{4h}).	b	Solution $\lambda(\mu)\xi$	Orientated crystal $\lambda(\parallel)\lambda(\perp)$	Circular Dichroism $\lambda(\mu)(\xi, -\xi_d)$	New assign- ment D_{4h}	a
I	${}^1E_g \longleftrightarrow {}^1A_{1g}$	E	625 33	625 625	- -	${}^1E_g \longleftrightarrow {}^1A_{1g}$	I
		P	610 35	- -	604 +0.8		
		E	- -	- -	- -		
		P	- -	- -	520 +0.12	${}^1A_{2g} \longleftrightarrow {}^1A_{1g}$	I
I	${}^1A_{2g} \longleftrightarrow {}^1A_{1g}$	E	444 25	- 424	- -	${}^1B_{2g} \longleftrightarrow {}^1A_{1g}$	II
		P	450 27	- -	- -		
II	${}^1B_{2g}, E_g \longleftrightarrow {}^1A_{1g}$	E	385 30	- -	- -		
		P	385 31	- -	392 +0.06	${}^1E_g \longleftrightarrow {}^1A_{1g}$	II

a. Parent Band in O_h ; b. E is trans- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$, P is trans- $[\text{Co}(-\text{pn})_2\text{Cl}_2]^+$

The old assignment is based on the orientated crystal study (143).

therefore assigned to the ${}^1A_{2g} \leftarrow {}^1A_{1g}$ transition. The assignment of the band at 385 mu. remained unchanged.

Wentworth and Piper⁽¹²⁴⁾ have measured the circular dichroism of trans-[Co(-pn)₂Cl₂]ClO₄ in methanol. They observed the same circular dichroism as is given in Table 16, but a very small shift ($\epsilon_1 - \epsilon_d = +.1$) in the base line of our measurement has produced two spurious circular dichroism bands at 520 mu. and 392 mu. and has obscured a small negative band at 461 mu. ($\epsilon_1 - \epsilon_d = -.1$). This transition is of course the ${}^1A_{2g} \leftarrow {}^1A_{1g}$ transition. The splitting of the E and A components of the first band is therefore about 5,100 cm⁻¹. A value of 5050 cm⁻¹ had previously been predicted⁽¹⁴⁶⁾ Wentworth and Piper⁽¹⁴⁷⁾ have interpreted these results in terms of the crystal field theory.

The trans-[Rh(-pn)₂Cl₂]Cl compound was also prepared in this work. The electronic spectrum and circular dichroism are given in Table 17. There have been no studies of the absorption spectrum of the single crystal of the trans-dichlorotetramminerhodium(III) complexes. The first absorption band is not resolved but it appears from the displacement of the circular dichroism band maximum that the forbidden transition lies at a lower energy than the allowed $E_g \leftarrow A_g$ transition. Wentworth and Piper found that this relationship between the energy levels existed in complexes of cobalt(III) with C_{4v} and D_{4h} symmetry⁽¹⁴⁷⁾. The assignments in Table 17 are based on the size of the circular dichroism bands. It appears from this work

Table 17

Electronic spectra of trans-dichlorobisdiaminerhodium(III) cations

Compound	Absorption		Circular Dichroism		Assignment
	$\lambda(\mu)$	ϵ	$\lambda(\mu)$	$(\epsilon_1 - \epsilon_d)$	
$[\text{Rhen}_2\text{Cl}_2]^+$	406	75			${}^1\text{E}_g, {}^1\text{A}_{2g} \leftarrow {}^1\text{A}_{1g}$
	286	130			${}^1\text{E}_g, {}^1\text{A}_{1g} \leftarrow {}^1\text{A}_{1g}$
$[\text{Rh}(-\text{pn})_2\text{Cl}_2]^+$	407	80	410	+0.6	${}^1\text{E}_g, {}^1\text{A}_{2g} \leftarrow {}^1\text{A}_{1g}$
	300	90	-	-	${}^1\text{B}_{2g} \leftarrow {}^1\text{A}_{1g}$
			270	+0.4	${}^1\text{E}_g \leftarrow {}^1\text{A}_{1g}$

that the rhodium(III) complexes are electronically analogous to cobalt(III) complexes. This has been found to be so in previous circular dichroism studies⁽⁷⁰⁾.

PART III

TETRAGONAL NICKEL(II) COMPLEXES

Lifschitz discovered that certain bisdiaminenickel(II) complexes showed interesting spectral and magnetic phenomena⁽⁵⁰⁾⁽⁶⁴⁾⁽¹²³⁾. For twenty years there was much discussion about the nature of these complexes. However the molecular structure of both the yellow and the blue isomers of one of these complexes has now been determined⁽¹⁴⁸⁾. The colour isomerism and the magnetic behaviour has been explained by a difference in the spin-degeneracy of the ground state in the two types of complex⁽¹⁴⁹⁻¹⁵²⁾. The assignment of the electronic transitions in these complexes, especially in the yellow diamagnetic complexes, is still uncertain.

We therefore prepared both the blue and yellow isomers of bis(+)propylenediaminenickel(II) perchlorate and the bis(-)stilbene-diaminenickel(II) perchlorate complexes. Both the O.R.D. curves and the circular dichroisms were measured. The Cotton effects of the (+)pn complexes were identical to those of the (-)stien complexes. This confirmed the absolute configuration of (-)stien. It also confirms that the energy levels of the nickel atom are similar in the corresponding complexes. Only the Cotton effects of the (+)propylenediamine complexes will be studied quantitatively because of the incomplete resolution of the stilbenediamine used.

The crystal structure of both the blue and the yellow $[\text{Ni}(\text{meso-stien})_2]$ dichloroacetate showed that the nickel atom lay

in the same plane as the puckered diamine rings and that the difference between the isomers was in the amount of tetragonal distortion. This confirmed what spectroscopists already believed⁽¹⁵³⁾. The rotational strengths of the Cotton effects must therefore arise by asymmetric induction. The blue complexes can be regarded as octahedral nickel(II) with a slight tetragonal distortion. They have three spin-allowed transitions: ${}^3T_{2g} \leftarrow {}^3A_{2g}$, ${}^3T_{1g} \leftarrow {}^3A_{2g}$ and ${}^3T_{1g} \leftarrow {}^3A_{2g}$ ⁽¹⁵⁴⁾. Only the first of these is magnetic-dipole allowed. The electronic spectra and the circular dichroisms of the blue and the yellow complexes are shown in Tables 18 and 19.

Table 18

The electronic spectra of Lifschitz salts

Complex	Solvent	Colour	λ	ϵ	λ	ϵ	λ	ϵ
$[Nipn_2]^{2+}$	ethanol	blue	958	6.2	580	5.0	360	10.8
$[Ni(meso-stien)_2]^{2+}$	acetone ^(a)	blue	970	6.5	600	7.0	370	12.0
$[Nipn_2]^{2+}$	nitromethane	yellow	445	15.5	-	-	-	-
$[Nistien_2]^{2+}$	nitromethane	yellow	445	50.5	-	-	-	-
$[Ni(meso-stien)_2]^{2+}$	nitromethane ^(a)	yellow	443	24	-	-	-	-

(a) Reference 156. This was the complex, whose structure was determined crystallographically⁽¹⁴⁸⁾.

λ in μ .

Table 19

Cotton effects in Lifschitz salts

Solvent ^(a)	Colour	$\lambda^{(b)}$	$\epsilon^{(b)}$	$\lambda^{(c)}$	$1^{-}d$	g
H ₂ O/EtOH	blue	580	5	575	-0.015	0.003
nitromethane	yellow	445	15	460	-0.15	0.01

(a) The salt used was [Ni(+pn)₂](ClO₄)₂; the O.R.D. curves of [Ni(-stien)₂](ClO₄)₂ are exactly parallel.

(b) Absorption values. λ in mu.

(c) Circular dichroism values. λ in mu.

g Kuhn dissymmetry factor.

Table 20.

g -factors for D[Ni(+pn)₃]²⁺

Transition	Absorption		Circular Dichroism		
	λ	ϵ	λ	$\epsilon, -\epsilon d^{(a)}$	g
${}^3T_{2g} \longleftrightarrow {}^3A_{2g}$	990	8	-	+0.18 ^(a)	0.23
${}^3T_{1g} \longleftrightarrow {}^3A_{2g}$	550	8	550	-0.04	0.005
${}^3T_{1g} \longleftrightarrow {}^3A_{2g}$	350	15	-	-	0.01

(a) The highest wavelength scanned for the circular dichroism was 890 mu., where the circular dichroism was still rising.

This table is taken from reference 157.

In octahedral nickel(II) complexes, the magnetic-dipole allowed, ${}^3T_{2g} \leftarrow {}^3A_{2g}$, transition, has been identified by the size of the Kuhn dissymmetry factor, g ,⁽¹⁵⁵⁾⁽¹⁵⁷⁾ and by a study of the polarised absorption spectra and of the fluorescence in symmetric complex ions⁽⁹⁾⁽¹⁵⁹⁾. In all these cases the magnetic-dipole allowed transition had the lowest energy of the three spin-allowed transitions. The circular dichroism of the blue bisdiaminenickel(II) complex was only measured between 600 mμ and 300 mμ. It therefore can be seen from Table 19 that the sizes of the g factors for the absorption bands at 580 mμ and 360 mμ are smaller than the value for magnetic-dipole allowed transitions. The ${}^3T_{2g} \leftarrow {}^3A_{2g}$ transition is therefore at a lower energy and gives rise to the absorption band at 958 mμ (Table 18). The similarity, with the exception of the magnitude of the circular dichroism, between the Cotton effects of the $[Ni(+pn)_2]^{2+}$ ion and the $[Ni(+pn)_3]^{2+}$ (157) ion is a confirmation of the smallness of the tetragonal distortion in the blue paramagnetic Lifschitz salts.

The yellow diamagnetic nickel(II) complexes have three spin-allowed transitions, ${}^1E_g \leftarrow {}^1A_{1g}$, ${}^1A_{2g} \leftarrow {}^1A_{1g}$ and ${}^1B_{1g} \leftarrow {}^1A_{1g}$, of which the first two are magnetic-dipole allowed and are polarised along the xy , and the z directions respectively. This polarisation of the two magnetic-dipole allowed transitions controls the borrowing of electric transition moment from the axial ligands. The xy polarised

magnetic-dipole transition can have a parallel vibrationally induced electric transition moment while the z polarised transition can have no such induced moment. Wentworth and Piper⁽¹²⁴⁾ have shown that this induced moment is quite considerable. It is therefore expected that the rotational strength of the ${}^1E_g \leftarrow {}^1A_{1g}$ transition will be greater than in the ${}^1A_{2g} \leftarrow {}^1A_{1g}$ transition. Only one circular dichroism band was observed. This band at 460 mμ is displaced to the long wavelength side of the only absorption band at 445 mμ. At 460 mμ, the Kuhn dissymmetry factor g is 0.01. This factor falls off sharply below 445 mμ. This is consistent with the postulate that the absorption band at 445 mμ contains at least two components. We suggest that the ${}^1E_g \leftarrow {}^1A_{1g}$ transition lies to the long wavelength side at about 460 mμ and the ${}^1A_{2g} \leftarrow {}^1A_{1g}$ transition lies on the shorter wavelength side of the absorption band. The question could be settled by the measurement of the polarised circular dichroism of a crystal of the complex.

There are several diamagnetic four-co-ordinate nickel(II) complexes. Recently diamagnetic forms of substituted bisacetyl-acetonatonickel(II) complexes have been reported⁽¹⁵⁸⁾. These red complexes were prepared by dehydrating the green dihydrate complexes in vacuo at 70°. As samples of bis(+)formylcamphornickel(II)dihydrate were available, the dehydration and isomerisation of this complex was attempted. There was no colour change on heating to temperatures as high as 160° in vacuo overnight. This is rather surprising as

the authors had attributed the change in colour and magnetism to the instability of the trimeric structure arising from steric hindrance. In chapter III of this thesis it was assumed that the chelate rings in (+)formylcamphor complexes interacted to a considerable extent.

CHAPTER V

STEREOSPECIFICITY IN COPPER(II) TARTRATE COMPLEXES

The complexes of copper(II) with tartaric acid in alkaline solution have received considerable attention because of their well-known use, as Fehling's reagent, for the analysis of sugars. The crystal structure of a tartrate complex has not been determined so structural information about the chelating properties of the tartrate anion is not available. Tartaric acid has four ionisable hydrogen atoms, two from the carboxyl groups and two from the α -hydroxyl groups. However, few workers who have studied the tartrate ion in alkaline solution seem to have realised the potential tetradentate nature of this ligand. It can reasonably be presumed that the tartrate anion will use a carboxyl group and an α -hydroxyl group to form a five-membered chelate ring similar to the α -amino-acidate chelate ring. The use of the two carboxyl groups to form a seven-membered chelate ring can be disregarded. The two hydroxyl groups could in strong alkaline solutions form a five-membered chelate ring. The puckering of any five-membered ring formed by an α -hydroxy-acid is expected to be negligible. The diol chelate ring will pucker in the manner of a diamine ring.

There have been several reports of stereospecificity in copper(II) tartrate complexes⁽⁵⁵⁾⁽¹⁶⁰⁾⁽¹⁶¹⁾⁽¹⁶²⁾. The amino-acidate complexes, bisasparaginatocopper(II)⁽⁵²⁾ and

bishistidinatocobalt(II), show a difference in the thermodynamic stability between the optically pure and the mixed isomers. In contrast no stereospecificity was observed in the bisalaninatocopper(II) complex. This difference in behaviour can be attributed either to the polydentate nature of the first two amino-acids or to the size of the substituents in the ligands. Observations on complexes of the type $[\text{Coen}_2\text{amino-acidate}]^{2+}$ (49) and $[\text{Coen}_2\text{tartrate}]^{2+}$ (163) suggest that the size of the ligand is an important factor.

A considerable amount of quantitative work has been done on copper(II) tartrate complexes. Cotton⁽¹⁶⁰⁾ has mentioned several times that the intensities of the blue colour of equimolar copper(II) (+)tartrate and copper(II) ($\pm$)tartrate solutions were different. Gheorghiu⁽¹⁶¹⁾ also noticed this difference but he observed that the absorption minima occurred at different wavelengths and that the absorbance of the racemic complex at the mercury green line (546 mμ) was 20% greater than the absorbance of the optically pure complex. Richtmeyer and Hudson⁽¹⁶²⁾ found that the rate of oxidation of an asymmetric sugar by the racemic Fehling's reagent was seldom the average of the rates of oxidation by the Fehling's reagents prepared from (+) and (-)tartaric acids, but often had a value outside the range of the rates of the optically pure reagents. This is evidence that copper(II) ($\pm$)tartrate cannot be considered as an equimolar mixture of copper(II) (+)tartrate and copper(II)

(~~m~~)tartrate. Fronaeus⁽⁵⁵⁾ has concluded from a very accurate study of the stability constants of copper(II) tartrate complexes that $\log K_1$ for the formation of copper (+)tartrate is 3.2 and $\log K_1$ for copper (⁺)tartrate is 3.0. He assumed that only monomeric species were present. However the species $[\text{Cu}(+\text{T})]^{n-}$ and $[\text{Cu}(-\text{T})]^{n-}$ must have the same stabilities as there can be no difference between the interaction of two enantiomers with a symmetric species such as the hydrated copper(II) ion. (The tartrate ion will be abbreviated as T for the rest of this chapter.) Fronaeus' experimental results are undoubtedly genuine but to explain the differences between optically pure and racemic copper(II) tartrates, complexes must be present where stereospecific interaction can occur. As the complexes contained copper(II) and tartrate in equimolar amounts, polymeric complexes must be postulated.

Polymeric species, such as $[\text{Cu}_3\text{T}_3(\text{OH})_6]^{6-}$ and $[\text{Cu}_4\text{T}_3(\text{OH})_5]_2^{6-}$, have been put forward to explain the variations of the pH of copper(II) tartrate solutions on the addition of alkali⁽¹⁶⁴⁾. Many authors have isolated compounds from alkaline copper(II) tartrate solutions. They have been forced to give polynuclear structures to these compounds in order to explain their analytical results. In contrast to this, Kirschner⁽¹⁶⁵⁾ has argued from the infra-red spectrum of solid copper(II) tartrate trihydrate that this compound is monomeric and has a tridentate tartrate ligand. Most of the

work on these complexes has been carried out with rather complex ratios of copper(II), tartaric acid and alkali. This makes the interpretation of the results very difficult.

In this work the stereospecificity of copper(II) tartrate complexes has been studied under controlled conditions. Equimolar amounts of copper(II) salts and tartaric acid were used, but the alkali concentration was varied from zero to ten times the equivalent amount of copper(II). The ratios of the components, over which the anomalous results were observed, could therefore be obtained and thus the stereospecificity could be related to the probable species in solution. The visible electronic spectrum was chosen as the best method for detecting the stereospecificity.

We observed that there is no difference between the two systems until more than two equivalents of alkali have been added. Up to this alkalinity the spectra were almost unchanged. When more than two equivalents of alkali were added the copper(II) (+)tartrate solution showed a tendency to give a fine precipitate. Similar behaviour was shown by the corresponding complexes with DL and L-glutamic acid at this point. The complexes with DL and L-malic acid gave an insoluble precipitate after the addition of three equivalents of alkali: Lifschitz⁽¹⁶⁶⁾ has prepared complexes of the type, $\text{Cu}[\text{Cu}(\text{aspartate})_2]$, which have the same stoichiometry as the solutions under discussion. He found that when these soluble complexes were boiled they were converted into insoluble complexes,

which had the same molecular formulae. This reaction can possibly be described:-



Das Sarma⁽¹⁶⁷⁾ has given a dimeric structure to the very insoluble glutamate complex. It is possible that the Tyndall effects shown by alkaline copper(II) tartrate solutions are associated with a similar polymerisation⁽¹⁶⁸⁾⁽¹⁶⁹⁾. When more than two equivalents of alkali were added to the copper(II) tartrate solutions, any precipitate which had appeared was immediately redissolved. This was not so with the insoluble copper(II) glutamates and the copper(II) malates. These compounds are insoluble even in large excesses of alkali. Yamada and Tamai⁽¹⁷⁰⁾ have stated that the ability of organic compounds to dissolve copper(II) in alkaline solution is related to the number of hydroxyl groups in the organic compound. This strongly suggests that in alkaline solutions the hydrogen atoms of these hydroxyl groups are removed and that the ionised groups become co-ordinated to the metal atom.

When more than two equivalents of alkali have been added, the solutions turned a deeper blue and the spectra of the optically pure and the racemic copper(II) tartrates were no longer similar. These differences which are described in Table 21 are most marked in the range three to four equivalents of alkali but they persist in large excesses of alkali. It was noticed that the Beer-Lambert

Table 21

The visible spectra of alkaline copper(II) tartrate solutions.

Equivalents of alkali per Cu^{2+}	Extinction coefficients at given wavelengths			
	546 m μ .		680 m μ .	
	DL	D	DL	D
0			6.4	6.6
1			8.7	8.7
2			12.0	-
2.2			15.3	-
2.4	1.7	.83	19.2	18.4
2.6	2.2	1.3	22.5	22.5
2.8	3.2	2.5	25.8	26.8
3.0	4.2	3.3	28.9	30.2
3.2	4.8	4.0	30.7	35.0
3.4	5.4	5.0	28.1	38.5
3.6	8.6	8.8	25.2	40.4
3.8	8.8	9.1	23.9	38.0
4.0	9.0	8.0	23.0	35.6
4.2				32.8
4.5				29.5
5.0			22.1	28.1
6.0			22.0	28.0
10.0			22.4	28.0

law was not obeyed by the tartrate complex in alkaline solution. Pfeiffer⁽¹⁶⁹⁾ has also noticed that the species in solution are dependent on the concentration of copper-containing ions in the solution. Over the range 2.5 to 5 equivalents of alkali there must be an equilibrium in solution between several complexes. We have noticed that other metal tartrate complexes do not obey the Beer-Lambert law. The "[Cr(+tartrate)₃]³⁻" ion, to which Mason⁽²⁵⁾ has assigned an absolute configuration is one of these. The magnetic susceptibility of the copper(II) tartrate solutions was not measured. However the E.S.R. spectra of the solutions were studied up to the addition of 2.5 equivalents of alkali. At this point the fine structure of the spectra was destroyed. This could be the result of an increase in the number of copper(II)-containing anions in solution and/or the production of complexes, in which there was considerable copper-copper interaction.

After the fifth equivalent of alkali had been added, there was no further change in the visible electronic spectra of the two complexes. In these solutions the absorption maximum of the (+)tartrato-complex is at 675 mμ and that of the racemic complex is at 650 mμ. The visually deeper blue solutions containing the racemic tartrate have weaker absorptions at band maxima than the apparently paler blue solutions of the active tartrates. The observations of Gheorghiu⁽¹⁶¹⁾ were confirmed.

In neutral solution, the pale blue copper(II) ions must

be almost octahedrally co-ordinated. As the alkali is added the four ionisable hydrogen atoms are removed, first from the carboxyl groups then from the hydroxyl groups. An anion is produced, which is potentially tetradentate. However this anion cannot be co-ordinated to one metal atom, using all four donor groups, because this is sterically impossible. The 1:1 ratio of copper(II):tartrate favours polynuclear species. Part of a polymer chain is shown in Figure 24. The polynuclear species contain octahedral copper(II), which has a considerable tetragonal distortion. This is the source of the deep blue colour of the alkaline solutions. In the region where the most marked stereospecific effects are seen, (2.5 to 5 equivalents of alkali), there must be an equilibrium between several species in solution. This equilibrium produces the deviations from the Beer-Lambert law. Solutions, which contain more than five equivalents of alkali, appear to be unchanged on the further addition of alkali. These solutions probably contain only one copper(II)-containing species. At a pH above pK_4 of tartaric acid, there can of course be no further ionisation of the tartrate anion. However, the stereospecific effects persist even with large excesses of alkali. Such effects were noticed by Cotton and Gheorghiu. This must reflect the different stereochemistry of the polymer chains. Only in structures which contain two or more

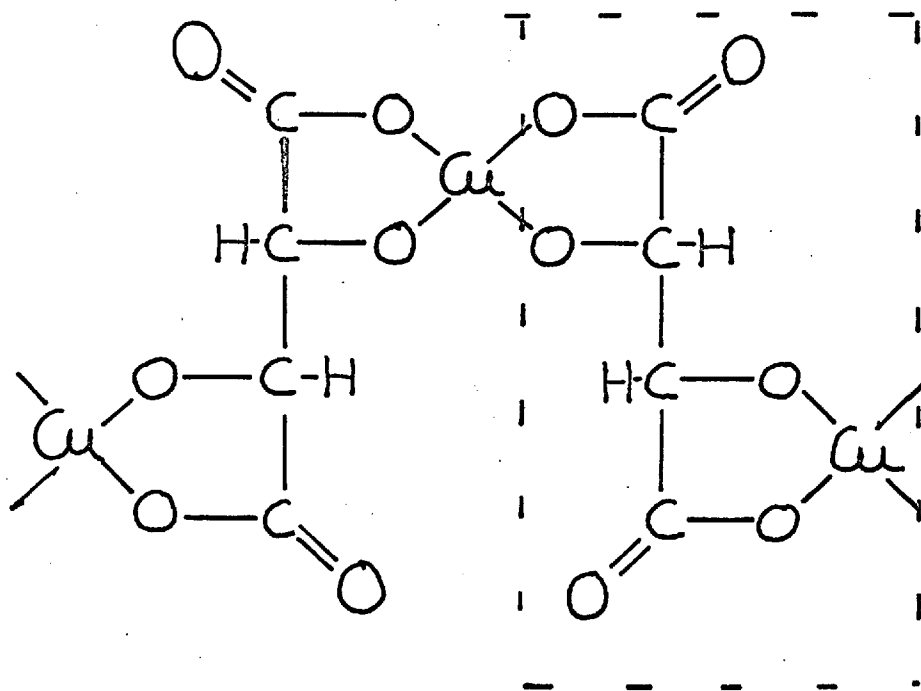


Figure 24.

A part of a copper(II) tartrate polymer chain, $(\text{CuT})_n^{2n-}$.
The enclosed section is the polymer unit $(\text{CuT})^{2n-}$.

Note: This is only a diagram. The two chelate rings in the same unit are not in the same plane.

asymmetric units, can there be different steric interactions. These different interactions produce different tetragonal distortions and metal-metal interactions in the polymers. The magnetic susceptibility of the alkaline solutions would give valuable information about these interactions.

It was mentioned above that (+)tartrate and (-)tartrate interacted with the symmetrical copper(II) aquo species in the same way. Therefore

$$(+T_{+}) = (-T_{+}) = \frac{1}{2}(+T_{+})$$

$$\text{and } [Cu(+T)]_{+} = [Cu(-T)]_{+}$$

$$\text{then } K_{1+} = K_{1-}$$

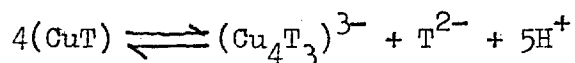
The unequal constants, which Fronaeus⁽⁵⁵⁾ reported, must refer to polymeric species and be constants made up of K_1 and constants of the type:-

$$\begin{aligned} K_{+}^n &= \frac{[Cu_n(+T)_n]}{[Cu(+T)]^n} \\ &= \frac{[Cu_n(+T)_n]}{K_{1+}[Cu]^n[+T]_{+}^n} \end{aligned}$$

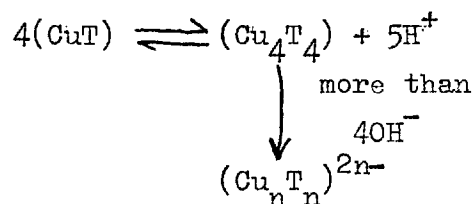
The inequality of the two constants obtained by Fronaeus suggests that copper (+)tartrate polymerises more readily than copper ($\pm$)tartrate. The copper(II) lactate complexes were examined but no stereospecific effects were found. The lactate anion is bidentate. This supports

the conclusion that the stereospecificity observed in the tartrate complexes is connected with polymeric species.

A large number of compounds have been isolated from alkaline solutions of copper(II) tartrate. Many of these compounds are polynuclear and contain copper(II) and tartrate in the ratio 1:1 or with an excess of copper(II) over the tartrate⁽¹⁶⁹⁾⁽¹⁷¹⁾. The compounds, which are isolated from a solution, do not necessarily predominate in the solution. However the isolation of such compounds shows that copper(II) complexes with α -hydroxy-acids can have polynuclear structures. The study of the magnetic susceptibility of these and similar compounds has detected the metal-metal interaction, which occurs in these complexes⁽¹⁷²⁾. Little work has been done on the nature of the copper(II)-containing species in solution but again polynuclear structures have been put forward to explain the experimental results⁽¹⁶⁴⁾⁽¹⁷³⁾. It should be mentioned here that polynuclear complexes have been suggested in solutions of copper(II) tartrate, which do not contain sufficient alkali to show the stereospecific effects, which we have observed. At 1.25 equivalents of alkali the equilibrium below has been postulated⁽¹⁶⁴⁾:-



We suggest the scheme:-



If this is the case, then stereospecificity must be associated only with degrees of polymerisation greater than four.

We have not attempted to evaluate formation constants because the presence of polymers and the almost unlimited number of copper(II)-containing species which may be present in alkaline solutions of copper(II) tartrate, makes the task impossible.

It was decided to examine the tartrato-oxovanadate(IV) complexes as a continuation of this work. These blue complexes are analogous to the copper(II) complexes and will for the rest of this chapter be referred to as the vanadyl tartrate complexes. The previous workers have assumed that the species present in alkaline solution are monomeric⁽¹⁷⁴⁾⁽¹⁷⁵⁾⁽¹⁷⁶⁾. The visible spectra of vanadyl (+)tartrate and vanadyl (⁺)tartrate were obtained over the same range of alkalinity as the copper(II) complexes. The results are shown in Table 22. Again the two complexes have identical spectra up to the addition of two equivalents of alkali. Beyond this point, stereospecific effects are observed and they are most marked in the range, three to four equivalents of alkali. Again the (+)tartrato-complex has the larger extinction coefficient. It is again suggested that the stereospecificity arises because of steric interactions in polynuclear complexes and that the (+)tartrato-complex polymerises more readily than the racemic complex. A new phenomenon was observed in the vanadyl complexes. Both the optically

Table 22

The visible spectra of alkaline vanadyl tartrate solutions.

Equivalents of alkali per Cu^{2+} VO^{++}	Extinction coefficients at given wavelengths					
	380 mu		586 mu		750 mu	
	DL	D	DL	D	DL	D
0	1.1	1.1	6.3	6.3	18.1	18.1
1	2.0	2.0	7.8	7.8	20.5	20.5
2	3.2	3.2	9.4	9.4	22.5	22.5
2.2	3.7	3.7	9.6	9.7	22.3	22.0
2.4	4.3	4.7	10.1	10.0	22.7	22.0
2.6	5.7	6.6	10.4	10.3	22.1	22.6
2.8	7.8	7.7	10.6	10.6	21.3	20.7
3.0 (1)	14.0	12.5	9.3	9.3	21.4	20.4
(2)	14.4	12.5	9.3	9.3	21.4	20.4
3.2 (1)	21.1	25.0	13.9	16.3	23.0	23.0
(2)	22.6	30.0	14.4	19.2		
3.4 (1)	27.7	35.0	16.3	22.2	24.2	24.0
(2)	29.2	43.5	16.8	25.0		
3.6 (1)	33.8	50.0	18.7	28.2	24.8	25.7
(2)	35.4	57.0	19.2	31.2		
3.8 (1)	40.0	63.5	21.3	33.8	25.5	27.0
(2)	41.6	69.0	21.9	37.0		
4.0 (1)	42.2	72.0	20.3	37.3	26.7	26.2
(2)	40.6	74.0	20.3	41.0		
5.0	45.0	39.0	22.5	18.0	36.0	6.0
6.0	44.6	32.0	22.7	14.6	32.0	6.4

(1) spectra measured immediately alkali was added;

(2) spectra measured after a period of five minutes.

pure and the racemic complexes, which contained more than three equivalents of alkali changed with time; the visible absorption bands increased in intensity on standing. In a fixed period, the increase was greater for the optically active complex than for the racemic complex. When more than five equivalents of alkali had been added, the complexes finally turned to a pale yellow-orange colour after a few days. This colour is very like that of certain vanadate (vanadium (V)) solutions. If four equivalents of alkali are added to the red solution of ammonium vanadate dissolved in an equimolar amount of tartaric acid, a pale blue colour develops. The "ageing" effect must therefore be due to an oxidation of the vanadium(IV) to vanadium(V), which is at least partly reversible. The "aged" solutions of the vanadium(IV) complexes could be restored to their original blue colour by the addition of acid. However the dependence of the redox reaction on the pH of the solution has not been fully studied yet. Fehling's reagent is also unstable but no change in the spectra of copper(II) tartrate complexes in alkaline solution was observed in one day. The decomposition of Fehling's reagent has not been studied.

The E.S.R. spectra of vanadyl (+)tartrate in alkaline solutions became very complex after the addition of two equivalents of alkali. In this it appears to be very similar to the copper(II) complex. The O.R.D. curves of vanadyl (+)tartrate were obtained over

a wide range of alkalinity. The vanadyl complexes, unlike the copper(II) complexes, showed Cotton effects between 600 mμ and 350 mμ. The Cotton effects were even observed when no alkali had been added. There must therefore be some association between the vanadyl ion and tartaric acid. When alkali was added the O.R.D. changed, reflecting the continuous variation of the species in solution with pH. Kar⁽¹⁷⁶⁾ reported that the circular dichroism of the ammonium vanadyl (+)tartrate was the inverse of the circular dichroisms of the sodium and potassium salts. These three salts are easily prepared as the monohydrates⁽¹⁷⁷⁾. The ammonium salt dissolved in water to give a paler solution than the sodium and potassium salts. This is probably a measure of the pH of the solutions of the dissolved salts, i.e. the ammonium solution is the least alkaline. However, the O.R.D. curves were similar and it is believed that the results of Kar⁽¹⁷⁶⁾ are erroneous. The vanadyl complexes appear to be entirely similar to the copper(II) complexes except in very alkaline solutions, in which the vanadyl complexes are much more unstable than the copper(II) complexes. The corresponding uranyl complexes were examined but no stereospecificity could be detected in them.

It has been customary in equilibrium studies to ignore the possible intervention of complexes of the type M_2L . However, Schwarzenbach⁽¹⁷⁸⁾ and others have pointed out that this is a dangerous

simplification, when a polydentate ligand is used. This work suggests that polymeric species dominate the behaviour of copper(II) and vanadyl tartrate complexes in alkaline solution. It would therefore be worthwhile to study many other metal tartrate complexes which have been reported.

Alkaline copper(II) tartrate solutions have been used for over a century for the analysis and detection of reducing sugars. The ratio of the components most commonly used is 1:4:12, copper(II):tartrate: alkali. This reagent is unstable. Many variations of Fehling's solution have been used in order to overcome this disadvantage. Both the organic acid component⁽¹⁷⁰⁾⁽¹⁷⁹⁾ and the alkali⁽¹⁸⁰⁾ have been changed. Tamada⁽¹⁷⁰⁾ has stated that any organic compound which can keep copper(II) salts soluble in an alkaline solution is a suitable substitute for tartaric acid in Fehling's reagent. Glucose itself will dissolve copper(II) salts in alkaline solution. The visible spectrum of the 1:1, copper(II):glucose complex in alkaline solution is given in Table 23. It is interesting that over the addition of about eight equivalents of alkali there is no change in the spectrum of the complex and also that the Beer-Lambert law is obeyed. The environment of the copper atom must therefore remain unchanged as the alkali is added and the complex must be stable. The stability of the closely related copper(II) gluconate complex is of the same order as the stability of the copper(II) E.D.T.A. complex.

Table 23

The visible spectra of the 1:1 complexes of copper(II) with (+)glucose and citric acid.

Equivalents of alkali per Cu^{2+}	Extinction coefficients at given wavelengths	
	(+)Glucose	Citric acid
	660 mu.	680 mu.
0	insoluble	7.2
1	"	11.6
2	"	20.5
2.2	"	22.3
2.4	"	24.8
2.6	37.0	27.0
2.8	36.7	29.5
3.0	37.2	31.6
3.2		34.5
3.4		36.5
3.5	38.4	
3.6		39.0
3.8		40.6
4.0	38.4	41.5
4.2		41.5
4.4		40.5
4.5	38.5	
5.0	38.3	39.5
6.0	37.3	
8.0	38.3	
10.0	37.5	

The concentration of the copper(II) in the glucose complex with 10 equivalents of alkali was half the concentration with only 2 equivalents of alkali.

Trommer in 1841 showed that the alkaline copper sulphate complexes of glucose and fructose could be used to distinguish between these two sugars⁽¹⁸²⁾. Fehling added tartaric acid to this mixture to improve the test but the tartaric acid is only an additive and is not absolutely necessary. This fact was rediscovered in a recent kinetic study of the oxidation of glucose by Fehling's reagent⁽¹⁸³⁾. It was of interest to ascertain the concentrations of alkali that are required in order that copper(II) tartrate and copper(II) sulphate are reduced by an equimolar amount of (+)glucose. When alkali was added to an equimolar mixture of copper(II) sulphate and (+)glucose, copper(II) hydroxide is precipitated but this precipitate is redissolved when 2.6 equivalents of alkali have been added. This deep blue solution gave a red precipitate of copper(I) oxide on warming. On the other hand, the copper(II) tartrate and citrate complexes required more alkali before they were reduced (see Table 24). The weaker oxidising power of the citrate complex (Benedict's reagent) with respect to the tartrate complex (Fehling's reagent) is well known⁽¹⁷⁹⁾. The small difference in oxidising power between the optically pure and the racemic Fehling's reagent is also confirmed⁽¹⁶²⁾. The reaction with these complexes becomes possible at the alkalinities, which give the most noticeable stereospecific effects. The mechanism possibly involves the transference of the copper atom from the tartrate polymer to the glucose anion. The copper(II) glucose complex then

Table 24

Reduction of copper(II) complexes by an equimolar amount of (+)glucose

Equivalents of alkali per Cu^{2+}	Colour of precipitate		
	D-tartaric acid	DL tartaric acid	citric acid
0-3	-	-	-
3.2	-	-	-
3.4	pale green	-	-
3.6	green	pale green	-
3.8	yellow	green	-
4.0	red	yellow	-
4.2	"	red	green
4.4	"	"	yellow
4.8	"	"	red
5.0	"	"	"

The colour is that developed after warming for five minutes at 70° .

undergoes an intramolecular redox reaction. Richtmeyer and Hudson⁽¹⁶²⁾ have shown with other reducing sugars that the relative configuration of the sugar and the Fehling's reagent affects the rate of the reaction. This suggests an intimate association between the copper(II) tartrate polymer species and the sugar molecule, in which steric interaction plays an important part. However there is still much work to be done on the mechanism of this reaction.

EXPERIMENTAL SECTION

The experimental work is described in sections, which are numbered to correspond with the discussion.

SECTION II

Microanalyses were by the Microanalytical Laboratory, Imperial College. Infra-red spectra were obtained on a Grubb-Parsons Spectrometer grating instrument and electronic spectra on a Perkin-Elmer, model 350, spectrophotometer. O.R.D. curves were obtained with a Bendix Polaromatic 62. instrument. Specific rotations were also measured on this instrument. Circular dichroisms were obtained on a Roussel-Jouan dichrograph.

Propylenediamine:-

This was resolved by the method of Dwyer, Garvan and Shulman⁽⁴³⁾. After 14 recrystallisations of (-)propylenediamine (+)tartrate, the recovered (-)propylenediamine had $[\alpha]_D = -34.4^\circ$. (0.8% in benzene). It was redistilled before use, the fraction boiling at 114-116° being collected. (+)Propylenediamine recovered from (+)[Co(+pn)₃]ClC₄H₄O₆ trihydrate had $[\alpha]_D = +34.1^\circ$. (0.7% in benzene).

Stilbenediamine:-

This compound was prepared by the method of Lifschitz and Bos⁽¹⁸⁴⁾ with the modifications of Williams and Bailar⁽¹⁸⁵⁾. The

racemic stilbenediamine (30g.) had m.p. 79° . lit. 83° . The diamine which was resolved with (+)tartaric acid had $[\alpha]_D = -62^{\circ}$. Lifschitz⁽¹⁸⁴⁾ reports $[\alpha]_D = -85^{\circ}$. An attempt was made to increase the resolution of the diamine but it was unsuccessful. Lifschitz observed that the diamine is unstable and is easily racemised.

Tris(-)propylenediaminerhodium(III) iodide hydrate:-

This white compound was prepared by the method used by Schmidtke⁽¹⁸⁶⁾ for the analogous compound of (+)propylenediamine. (Found: I, 52.9; Calc. for $\text{RhC}_9\text{H}_{32}\text{N}_6\text{OI}_3$: I, 52.70%). The visible spectrum in water showed absorption maxima at 300 m μ $\epsilon = 280$, 261 m μ $\epsilon = 7,500$ and 225 m μ $\epsilon = 35,000$. The infra-red spectrum, measured as a nujol mull, showed the presence of a water of hydration. Specific rotations; $[\alpha]_D = +94.5^{\circ}$ and $[\alpha]_{300} = +1,475^{\circ}$.

Tris(-)propylenediaminechromium(III) chloride:-

This yellow solid was prepared by a modification of the method of Rollinson and Bailar⁽¹⁸⁷⁾. Anhydrous chromium(III) sulphate (2g.) was heated with (-)propylenediamine (3ml.). The reaction product was extracted with methanol containing a little dilute hydrochloric acid. Tetrahydrofuran was added slowly to the yellow-orange extract, precipitating a product which contained sulphate ions (revealed by the infra-red spectrum). The product was therefore dissolved in dilute hydrochloric acid and the solution was treated with barium chloride. The filtered solution was then

treated with tetrahydrofuran, the precipitate was collected and then extracted with methanol (25 ml.) containing concentrated hydrochloric acid (0.5 ml.). The complex was reprecipitated from the methanolic solution with ether. This reprecipitation was repeated twice, when tris(-)propylenediaminechromium(III) chloride was obtained as a yellow solid. (Found: Cl, 27.95; Calc. for $\text{CrC}_9\text{H}_{30}\text{N}_6\text{Cl}_3$: Cl, 28.18%). The visible spectrum in water was identical with that given in the literature⁽¹⁸⁸⁾. Specific rotation: $[\alpha]_{500} = -322^\circ$.
trans-Dichlorobis(-)propylenediaminecobalt(III)bis-aquohydrogen chloride:-

This green compound was prepared by the method of Werner and Frohlich⁽¹⁸⁹⁾ for the analogous compound of (+)propylenediamine. (Found: weight loss at 110° , 28.1; Required: 28.0%). The visible spectrum of the compound in dilute hydrochloric acid agreed with that reported by Basolo⁽¹⁴⁴⁾.

trans-Dichlorobis(-)stilbenediaminecobalt(III) chloride:-

This green crystalline solid was prepared by the method of Williams and Bailar⁽¹⁸⁵⁾. (Found: Cl, 16.40; Calc. for $\text{CoC}_{28}\text{H}_{34}\text{N}_4\text{OCl}_3$: Cl, 17.53%). The visible spectrum measured in alcohol showed an absorption maximum at 607 mμ. $\xi = 65$ and shoulders at 450 mμ. and 390 mμ. This is very similar to the spectrum of trans- $[\text{Co}(\text{pn})_2\text{Cl}_2]\text{Cl}$ recorded by Basolo⁽¹⁴⁴⁾, which showed a maximum at 610 mμ. $\xi = 34$ and a shoulder at 450 mμ.

Bis(+)propylenediaminenickel(II) perchlorate trihydrate:-

The blue crystals of this were prepared by the method of Lifschitz⁽⁶⁹⁾. (Found: C, 15.41; H, 5.70; Calc. for $\text{NiC}_6\text{H}_{26}\text{N}_4\text{Cl}_2\text{O}_{11}$: C, 15.65; H, 5.65%.) The visible spectrum in 50% aqueous alcohol showed absorption maxima at 952 m μ . ϵ = 6.2, 560 m μ . ϵ = 4.8 and 350 m μ . ϵ = 10.8. The trihydrate was heated in an oven overnight at 70°. This dehydration produced the yellow isomer.

The yellow $[\text{Ni}(+pn)_2](\text{ClO}_4)_2$ was dissolved in nitromethane. The visible spectrum showed absorption maxima at 875 m μ . ϵ = 3.6 and 445 m μ . ϵ = 19.6. The O.R.D. curve of the blue isomer was identical with that described in the literature⁽⁴⁴⁾.

Bis(-)stilbenediaminenickel(II) perchlorate:-

This yellow powder was prepared by the method of Lifschitz and Bos⁽⁶⁴⁾. (Found: C, 48.86; H, 4.83; Calc. for $\text{NiC}_{28}\text{H}_{32}\text{N}_4\text{Cl}_3\text{O}_8$: C, 48.34; H, 4.70%.) The visible spectrum measured in nitromethane showed an absorption maximum at 450 m μ . ϵ = 50.5. The O.R.D. curve of this compound was identical with that described in the literature⁽⁶⁴⁾.

SECTION III

The microanalyses in this and the following sections were by the Microanalytical Laboratory, Sheffield University. The electronic spectra were measured on a Perkin-Elmer Ultracord spectrophotometer

Trisglycinatocobalt(III):-

The violet α -isomer was prepared by the method⁽⁷⁷⁾ of Ley from cobalt(III) hydroxide. Its properties agreed well with those reported⁽⁷⁸⁾. A saturated aqueous solution (10 ml.) of this isomer was chromatographed on a column of potato starch (400 g.). Krebs has mentioned⁽⁸¹⁾ this method of resolution. The first eluate contained $\alpha(+)\text{Co}(\text{glycine})_3$, whose optical rotatory dispersion curve is shown in Figure 15.

The red β -isomer was prepared from hexamminecobalt(III) chloride, following the literature method⁽⁸⁰⁾.

Tris L-alaninatocobalt(III):-

The following preparative methods were used: The details were as given⁽⁸⁰⁾.

- 1) From cobalt(III) hydroxide:- This method gives predominantly violet isomers.
- 2) From hexamminecobalt(III) chloride:- This method gives only the water-insoluble $\beta(+)$ -isomer. The filtrate, after the $\beta(+)$ -isomer had been removed, was examined. Only cobalt(II) compounds were detected. Strangely enough, when racemic alanine was used in this preparation instead of L- α -alanine, then considerable amounts of an α -isomer were isolated, which we suppose to contain optically mixed ligands, i.e.

DL- α -Co(L-ala)(D-ala)₂ and/or DL- α -Co(L-ala)₂(D-ala).

3) From sodium triscarbonatocobaltate(III):- All four isomers can be isolated from the reaction products. However, the two violet isomers predominate.

Isolation of the isomers:-

1) $\beta(+)$ trisL-alaninatocobalt(III):-

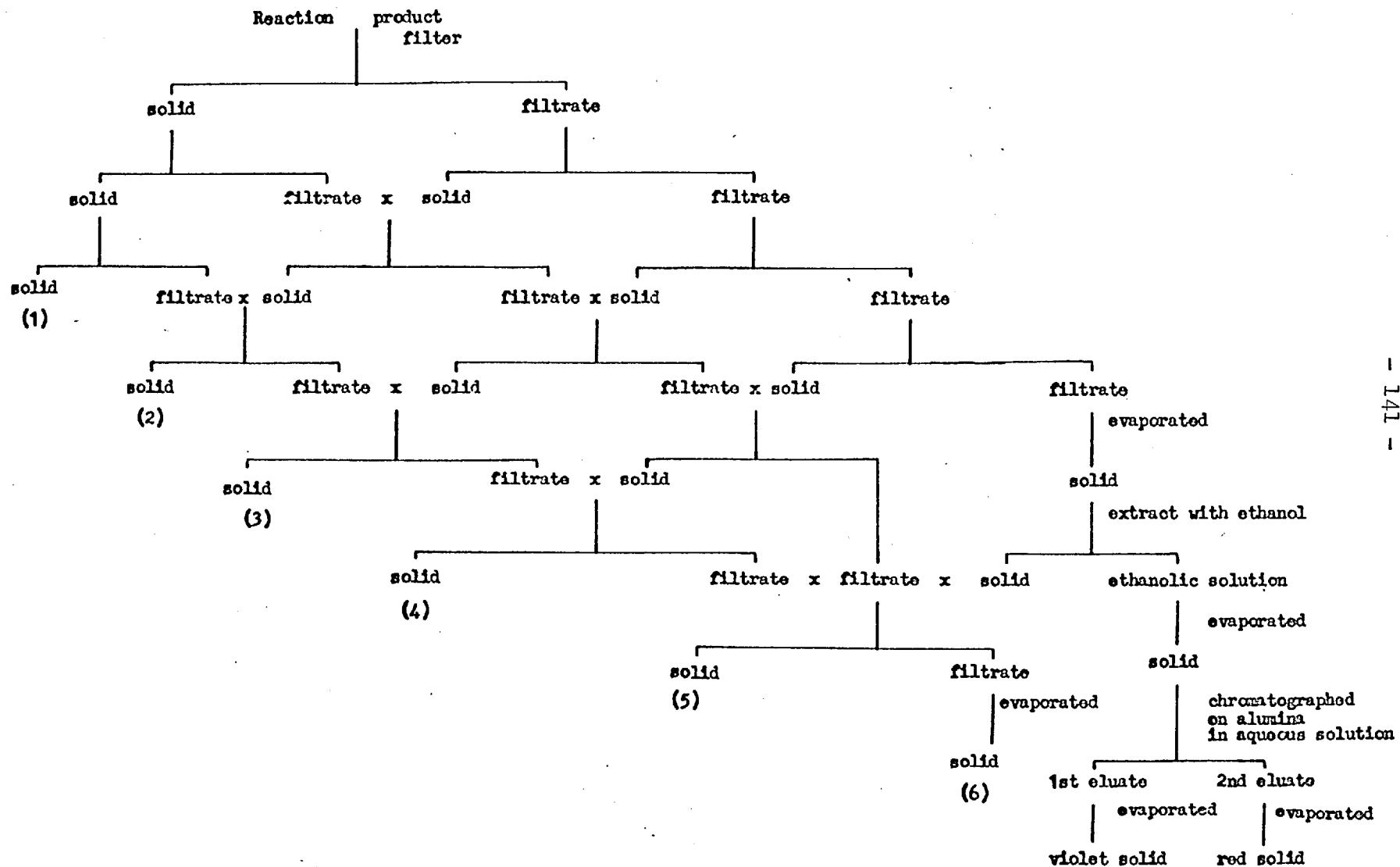
This water-insoluble pink micro-crystalline solid was separated from the other isomers by filtration. It was recrystallised from 50% sulphuric acid. The solid was reprecipitated from the acid solution by the addition of water. Several fractions were obtained by this method. Their specific rotations are given below.

$$[\alpha]_{500} = -1060^{\circ}, -850^{\circ} \text{ and } -793^{\circ}.$$

The specific rotation of the acid solution before precipitation was $[\alpha]_{500} = -1255^{\circ}$. We attribute the slight variations in optical properties of this isomer to varying degrees of polymerisation.

2) The violet α -isomers:-

The solid product from the preparation using sodium triscarbonatocobalt(III) was extracted with large volumes of boiling water. The violet isomers and the red $\beta(-)$ isomer were thus dissolved. The resulting solution was fractionally crystallised according to the scheme below:-



To ascertain the optical purity of the $\alpha(-)$ isomer we refractionated the entire fraction 6, dissolved in 50% aqueous ethanol, by successive additions of, first acetone and subsequently ether. The properties of the fractions, which were thus precipitated, are given below:-

Fraction	Solvent	$[\alpha]_{476}$
original material (Fraction 6)	-	+ 1,340°
1	acetone	+ 1,190°
2	acetone	+ 1,180°
3	ether	-
4	ether	+ 1,220°
5	ether	+ 1,330°

$\beta(-)$ -trisL α -alaninatocobalt(III):-

This water-soluble isomer was separated from the alcohol-soluble $\alpha(-)$ -isomer by chromatography on alumina. In aqueous solution the red isomer is more strongly absorbed and is thus eluted after the violet isomer. The aqueous solution of this red $\beta(-)$ -isomer was evaporated to a small volume. Ethanol was added to this solution and the solution was again evaporated to a small volume. Fine red crystals of the $\beta(-)$ -isomer were formed on standing at low temperature. The crystals were removed from the solution by filtration. They were washed with alcohol and with ether and were then dried in a vacuum desiccator.

Properties of the isomers.

$\alpha(+)$ -trisL-alaninatocobalt(III) monohydrate:-

A violet crystalline solid sparingly soluble in water. (Found: C, 31.68; H, 5.87; N, 12.32; Calc. for $\text{CoC}_9\text{H}_{20}\text{N}_3\text{O}_7$: C, 31.66; H, 5.86; N, 12.31%.) Specific rotations:- $[\alpha]_{\text{D}} = +847^\circ$, $[\alpha]_{546} = 0$; $[\alpha]_{476} = -2960^\circ$. Lifschitz's values⁽⁴⁵⁾ for this compound were:- $[\alpha]_{\text{D}} = 1845^\circ$, $[\alpha]_{546} = 0$; $[\alpha]_{476} = -2750^\circ$. Absorption maxima occurred at:- 375 mu., $\epsilon = 151$ and 545 mu., $\epsilon = 104$.

$\alpha(-)$ -trisL α -alaninatocobalt(III) monohydrate:-

A violet non-crystalline powder which is very soluble in water and is sparingly soluble in alcohol. The infra-red spectrum of this compound has an absorption peak at 3500 cm^{-1} . This confirms the presence of a molecule of water of crystallisation. A crystalline sample was obtained from ethanol. (Found: C, 31.64; H, 5.47; N, 12.68; $\text{CoC}_9\text{H}_{20}\text{N}_3\text{O}_7$ requires C, 31.66; H, 5.86; N, 12.31%.) (Lifschitz's α' -isomer was allegedly anhydrous.) The specific rotations are $[\alpha]_{\text{D}} = -660^\circ$, $[\alpha]_{546} = 0$, $[\alpha]_{476} = +1352^\circ$. Lifschitz's values⁽⁴⁵⁾ for his α' -isomer were:- $[\alpha]_{\text{D}} = -590^\circ$, $[\alpha]_{546} = -50^\circ$, $[\alpha]_{476} = +900$. Lifschitz demonstrated by cryoscopy that his α' -isomer was monomeric. Absorption maxima occurred at:- 375 mu. $\epsilon = 96$ and 540 mu. $\epsilon = 60$.

$\beta(+)$ -trisL α alaninatocobalt(III):-

A pink crystalline solid, which is insoluble in water and only soluble in 50% sulphuric acid. Cryoscopic studies in concentrated sulphuric acid have ambiguous results owing to the possibility of a polymeric structure for this isomer, which is also suggested by the small variations in $[\alpha]$ values found. (Found: C, 33.39; H, 5.38; N, 12.83; Calc. for $\text{CoC}_9\text{H}_{18}\text{N}_3\text{O}_6$: C, 33.44; H, 5.56; N, 13.00%.) Specific rotations:- $[\alpha]_D = +285^\circ$, $[\alpha]_{546} = -770^\circ$, $[\alpha]_{500} = -1255^\circ$. Lifschitz's values⁽⁴⁵⁾ $[\alpha]_D = -45^\circ$, $[\alpha]_{546} = -690^\circ$, $[\alpha]_{500} = -1720^\circ$. Absorption maxima occurred at:- 375 mu. with $\xi = 127$ and 516 mu.

$\xi = 149$. Although slight differences were found for the rotations of samples obtained in different ways, we feel that this arises from the probably polymeric nature of the compound.

$\beta(-)$ -trisL α alaninatocobalt(III):-

A pink crystalline compound, which is soluble in water and sparingly soluble in ethanol. (Found: C, 33.04; H, 5.51; N, 13.00; $\text{CoC}_9\text{H}_{18}\text{N}_3\text{O}_6$ requires C, 33.44; H, 5.56; N, 13.00%.) Specific rotations: $[\alpha]_D = -990^\circ$, $[\alpha]_{546} = 0^\circ$, $[\alpha]_{500} = +1870^\circ$. Absorption maxima occurred at: 376 mu., $\xi = 148$ and 516 mu., $\xi = 192$. All four trisL α alaninatocobalt(III) complexes are stable in acid solutions but are decomposed on warming in alkaline solution.

Interconversions and Equilibria

α (+)-trisglycinatocobalt(III):-

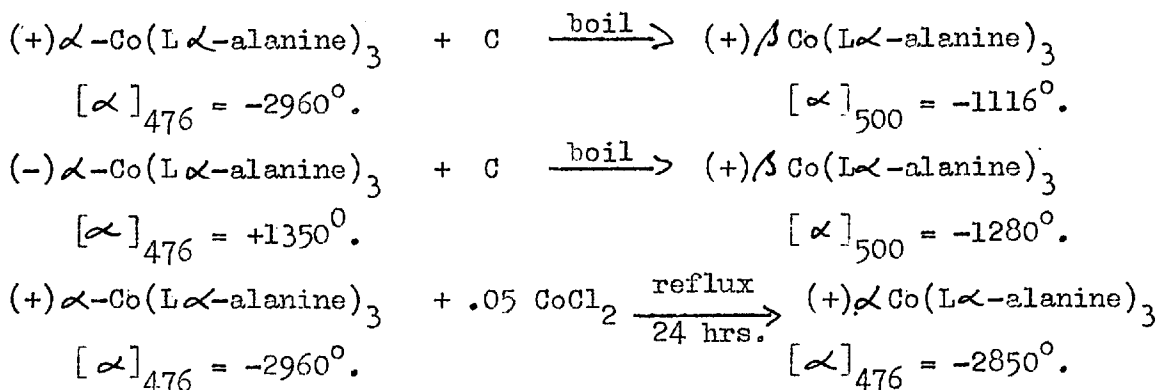
A dilute solution (10 ml.) of this compound $[\alpha]_{476} = -300^\circ$, was boiled with a very small amount of activated charcoal. The optical activity had disappeared after two minutes boiling. Therefore equilibration is achieved in a short time. The unresolved compound (0.5 g.) in water (25 ml.) was then boiled for three hours with activated charcoal. There was no change in the visible spectrum. Although small amounts of cobalt(II) compounds were detected in the final solution, no red isomer had formed, so that the equilibrium is almost entirely on the side of the violet isomer.

β trisglycinatocobalt(III):-

A dilute aqueous solution of this compound was boiled for three hours with a small amount of activated charcoal. The visible spectrum of the final solution showed that the β -isomer had been largely converted into the α -isomer.

α -trisalaninatocobalt(III):-

When this compound is boiled with activated charcoal, the β -isomer is quickly precipitated. The filtrate contains cobalt(II) compounds. The two diastereoisomers of the violet α -complex were therefore treated in the same way to see which β -isomer was produced. The results are indicated below:-



The $\alpha(+)$ -isomer is therefore almost unaffected by boiling in water for 24 hours in the presence of cobalt(II) ions.

Also, in case the small amount of $\beta(-)$ -isomer obtained by chromatography in ethanol on alumina was an artefact, we treated both $\alpha(+)$ and $\alpha(-)$ -isomers in aqueous ethanol with alumina, but no isomerisation occurred.

Determination of equilibrium amounts:

1) From the preparation using sodium triscarbonatocobaltate(III):-
The fractions from the fractional crystallisation were weighed (see scheme) and the amounts of the two diastereoisomers were calculated using the relationship below:-

$$\begin{aligned}
 [\text{Co}][\alpha] &= [\text{Co}_D][\alpha_D] + [\text{Co}_L][\alpha_L] \\
 \frac{[\text{Co}_D]}{[\text{Co}_L]} &= \frac{[\alpha_L] - [\alpha]}{[\alpha] - [\alpha_D]}
 \end{aligned}$$

where $[\text{Co}]$, $[\text{Co}_D]$ and $[\text{Co}_L]$ are the concentrations of the original unfractionated material and the optically pure D and L compounds respectively, and $[\alpha]$, $[\alpha_D]$ and $[\alpha_L]$ are their specific rotations

at 476 mu. The results of these calculations are given in Table 25.

2) From cobalt(III) hydroxide:- The stereospecificity was calculated from the rotation of the filtrate, which contained all the α -isomers, before the fractional crystallisation was carried out. The unreacted cobalt(III) hydroxide was boiled with water for a considerable time (ca. 3 hours) to make sure that all of the rather insoluble α (+)-isomer is taken into solution. This solution will contain the β (-)-isomer also but its amount, less than 2% of α -isomer, is too small to affect the result. The total amount of the α -isomers in solution was determined by gravimetric analysis for cobalt using α -nitroso β -naphthol. The solution of the complex was evaporated to dryness. A small sample of the solid was dissolved in concentrated hydrochloric acid to see if any cobalt(II) compounds were present. No cobalt(II) was detected. Therefore the analytical result of 0.4213 g. cobalt in 1000 ml. solution was taken with the specific rotation of the mixture. $[\alpha]_{476} = -206^\circ$ to calculate that the ratio of the α (+)-isomer to the α (-)-isomer in the initial mixture was:-

$$\frac{\alpha(+)}{\alpha(-)} = \frac{47.7}{52.3}$$

Tris(α -alaninato)rhodium(III)

1) From rhodium(III) hydroxide:- Rhodium(III) chloride trihydrate (2.67 g.) was dissolved in water. (30 ml.) Sodium bicarbonate (3 g.) was added to this solution until there was no effervescence and a

Table 25.

Fractional crystallisation of α -Co(L-alanine)₃

Fraction	$[\alpha]_{476}$	Weight (g.)	Composition	
			$\alpha(+)$ (g.)	$\alpha(-)$ (g.)
1	-2,460°	1.163	1.163	0.000
2	-2,850°	0.674	0.660	0.014
3	-2,570°	0.443	0.402	0.041
4	-2,750°	0.318	0.303	0.015
5	+ 435°	0.527	0.116	0.410
6	+1,190°	1.560	0.160	1.400
alcohol soluble	+1,350°	<u>0.380</u>	<u>0.000</u>	<u>0.380</u>
Totals		5.065	2.804	2.260

$$\text{whence } \frac{\alpha(+)}{\alpha(-)} = \frac{55.5}{44.5}$$

yellow precipitate had formed on warming the solution. L α -alanine (2.7 g.) was then added and the mixture was refluxed for two hours when the reaction was assumed to be complete. The white crystalline solid which had formed was collected. It was extracted with several portions (4 x 200 ml.) of boiling water, which after removal of this water insoluble compound (final weight 0.60 g.) were added to the original filtrate. The filtrate was then fractionally crystallised. This gave 4 fractions of an off-white solid whose total weight was 1.16 g. A yellow solution remained, from which no further solids could be crystallised. The visible spectrum and optical rotatory dispersion of this solution showed that it contained only unreacted starting material.

2) From rhodium(III) iodide:- This preparation was similar to the method above. Rhodium(III) iodide and anhydrous sodium carbonate were used instead of the rhodium(III) chloride and sodium bicarbonate. The two compounds, which have been designated the $\beta(-)$ and $\beta(+)$ -isomers of trisL-alaninatorrhodium(III), were separated by the method described above.

Fractional crystallisation of $\beta(+)$ trisL-alaninatorrhodium(III):-

This was carried out in the same way as the fractional crystallisation of $\alpha(+)$ trisL-alaninatocobalt(III). Table 26 gives the specific rotations of the fractions, with that of the previously removed $\beta(-)$ -isomer for comparison. The rapid decrease of $[\alpha]_{300}$

Table 26

Fractional crystallisation of water-soluble isomers of Rh(L-alanine)₃

Fraction	$[\alpha]_{300}$	Nature
1	+2,230°	$\beta(+)$
2	+ 840°	Mixed α
3	+ 490°	"
4	+ 195°	"
pure L-alanine	+ 74°	
water-insoluble	- 795°	$\beta(-)$

suggests that the later fractions are either a mixture of the two Δ -diastereoisomers or, less likely, of one Δ -isomer and free L-alanine. Two types of crystal in fraction 4 could be seen clearly under the microscope. The spectrum of fraction 4 is given in Table 27; all the bands observed may be assigned to an Δ -isomer.

The assignment of isomeric structures to the complexes of rhodium(III) is supported by infra-red spectra as shown in Table 27.

Properties of the isomers.

$\beta(+)$ trisL Δ alaninatorhodium(III):-

An off-white solid, which is sparingly soluble in water. (Found: C, 29.57; H, 4.72; $C_9H_{18}N_3O_6Rh$ requires: C, 29.43; H, 4.91%.) Specific rotations:- $[\alpha]_D = +256^\circ$, $[\alpha]_{546} = +223^\circ$ and $[\alpha]_{300} = +2230^\circ$. Absorption maxima occurred at 339 μ . $\zeta = 400$ and 286 μ . $\xi = 345$. The infra-red spectrum of this isomer is very similar indeed to that of the $\beta(-)$ -isomer, which is given in Table 27.

$\beta(-)$ trisL Δ alaninatorhodium(III):-

An off-white crystalline solid, which is completely insoluble in water but dissolves in 50% sulphuric acid. (Found: C, 28.78; H, 5.02; N, 11.52; $C_9H_{18}N_3O_6Rh$ requires: C, 29.43; H, 4.81; N, 11.45%.) Specific rotations:- $[\alpha]_{500} = -92^\circ$ and $[\alpha]_{300} = -795^\circ$. Absorption maxima occurred at 338 μ . $\zeta = 440$ and 285 μ . $\xi = 382$.

Mixture of Δ -trisL Δ alaninatorhodium(III) isomers:-

A pale yellow solid, which is soluble in water. (Found: C, 28.00; H, 4.77; $C_9H_{20}N_3O_7Rh$ requires C, 28.05; H, 5.19%.)

Table 27

Infra-red spectra of isomers of M(L-ala)₃

$\alpha(+)\text{Co(L-ala)}_3$ (cm. ⁻¹)	$\alpha(+)\text{Rh(L-ala)}_3^a$	$\beta(+)\text{Co(L-ala)}_3$	$\beta(-)\text{Rh(L-ala)}_3$
3500 m	3450 s		
3200 s	3200 s	3250 s	3200 s
3100 sh	3100 s	3120 s	3100 s
1660 vs	1652 vs	1650 vs	1640 vs
1600 sh	1600 s	1590 s	1580 s
1400 s			
1370 vs	1365 vs	1380 vs	1360 vs
1340 s	1340 s	1360 vs	1340 s
1300 s	1295 sh		
1280 s	1280 s	1275 vs	1260 s
1265 s	1278 sh	1255 m	1240 m
1230 s	1238 m		
1210 s	1205 m	1200 m	1190 m
1155 m			
1120 s	1115 m	1110 m	1100 m
1085 m	1085 w		
1070 m	1065 w		
1035 m			
1020 w	1020 w	1030 w	1010 w
935 m	925 m	925 m	920 m
870 s	863 s	860 s	855 s
835 w	845 sh		
810 w	820 w	815 w	820 m
785 w		785 w	
760 s	760 s	745 w	755 sh
735 m	735 m	730 m	740 m

a. This is fraction 4. from Table 27.

Absorption maxima occurred at 335 mu. $\lambda = 265$ and 287 mu. $\lambda = 322$. The infra-red spectrum showed a band at $3,450\text{ cm}^{-1}$ which confirms the presence of a molecule of water of crystallisation.

TrisL-glutamato-cobaltate(III) compounds:-

These compounds were prepared by the methods of Lifschitz⁽⁴⁷⁾. They are here referred to by Lifschitz's nomenclature.

Silver D Δ -trisL-glutamato-cobaltate(III):-

A pale violet solid. (Found: Ag, 40.05; Calc. for $\text{Ag}_3\text{CoC}_{15}\text{H}_{21}\text{N}_3\text{O}_{12}$: Ag, 39.58%) The visible spectrum showed absorption maxima at 525 mu. and 375 mu.

Lead D Δ -trisL-glutamato-cobaltate(III):-

A pale violet solid. (Found: Pb, 38.69; Calc. for $\text{Pb}_3\text{Co}_2\text{C}_{30}\text{H}_{42}\text{N}_6\text{O}_{24}$: Pb, 38.62%.) The visible spectrum showed absorption maxima at 525 mu. and 375 mu.

Lead D δ -trisL-glutamato-cobaltate(III):-

A dark red solid. (Found: Pb, 38.37; Calc. for $\text{Pb}_3\text{Co}_2\text{C}_{30}\text{H}_{42}\text{N}_6\text{O}_{24}$: Pb, 38.62%.) The visible spectrum showed absorption maxima at 525 mu. and 370 mu.

Silver L Δ -trisL-glutamato-cobaltate(III):

A pale violet solid. (Found: Ag, 36.43; Calc. for $\text{Ag}_3\text{CoC}_{15}\text{H}_{21}\text{N}_3\text{O}_{12}$: Ag, 37.93%.) The visible spectrum showed absorption maxima at 525 mu. and 370 mu.

Bispyridinesilver(I) Lβ-trisL-glutamato-cobaltate(III):-

A dark red solid. (Found: Ag, 29.18; Calc. for $\text{Ag}_3\text{CoC}_{45}\text{H}_{51}\text{N}_9\text{O}_{12}$: Ag, 25.06%.) The visible spectrum showed absorption maxima at 520 mμ. and 370 mμ.

Extinction coefficients are not quoted because of the instability of some of the solutions and the difficulty in completely converting the silver and lead salts to soluble sodium salts.

Analyses:

Silver was analysed gravimetrically as silver chloride by the method given by Vogel⁽¹⁹⁰⁾. Lead was analysed gravimetrically as lead sulphate by the method given by Vogel⁽¹⁹⁰⁾.

Equilibration:

Silver D~~α~~-trisL-glutamato-cobaltate(III):-

A small amount (1 g.) of this complex was taken into solution as the sodium salt. The solution was refluxed for ten minutes with a very small amount (.01 g.) of activated charcoal, but there was no change in the O.R.D. curve of the solution. Prolonged refluxing produced cobalt(II) compounds. A similar amount of the silver salt was dissolved in an aqueous solution of pyridine (100 ml. of a 5% solution). The solution was warmed at 80° overnight. There was no change in the O.R.D. curve of the solution.

Trisacetylacetonatocobalt(III):-

This green crystalline compound was prepared by the method described in the literature⁽¹⁹¹⁾. It had the properties mentioned therein. The visible spectrum in 95% ethanol showed only one d-d absorption maximum at 596 mμ. $\epsilon = 140$.

(+)Hydroxymethylcamphor:-

This white crystalline compound was prepared by the method of Claisen⁽⁹⁰⁾. m.p. 71°. lit. 70-76°. $[\alpha]_{500} = +280^\circ$. Lifschitz⁽⁹²⁾ gives $[\alpha]_{500} = +300^\circ$ in ethanol.

(-)Tris(+)formylcamphorcobalt(III):-

This green non-crystalline compound was prepared by the method of Lifschitz⁽⁹¹⁾. The green ligroin-soluble product was chromatographed on a 50 cm. column of alumina in ligroin. The majority of the material passed straight through the column in one band. A small amount of dark green material was left at the top of the column. This was identified as the polymer described by Lifschitz. The eluate was concentrated and a green solid was precipitated.

(Found: C, 66.36; H, 7.40; Calc. for $\text{CoC}_{33}\text{H}_{45}\text{O}_6$: C, 66.45; H, 7.55%.)

The visible spectrum in chloroform showed only one d-d absorption maximum at 608 mμ. $\epsilon = 118$. Mason quotes 607 mμ. $\epsilon = 130$.⁽¹⁷⁾ and 610 mμ. $\epsilon = 174$.⁽²⁵⁾ The specific rotations in methanol are:

$[\alpha]_D = -2,710^\circ$, $[\alpha]_{500} = -3,750^\circ$. Lifschitz gives⁽⁹²⁾ $[\alpha]_D = -500^\circ$, $[\alpha]_{500} = -2,623^\circ$. A small portion (.03 g.) of the compound was

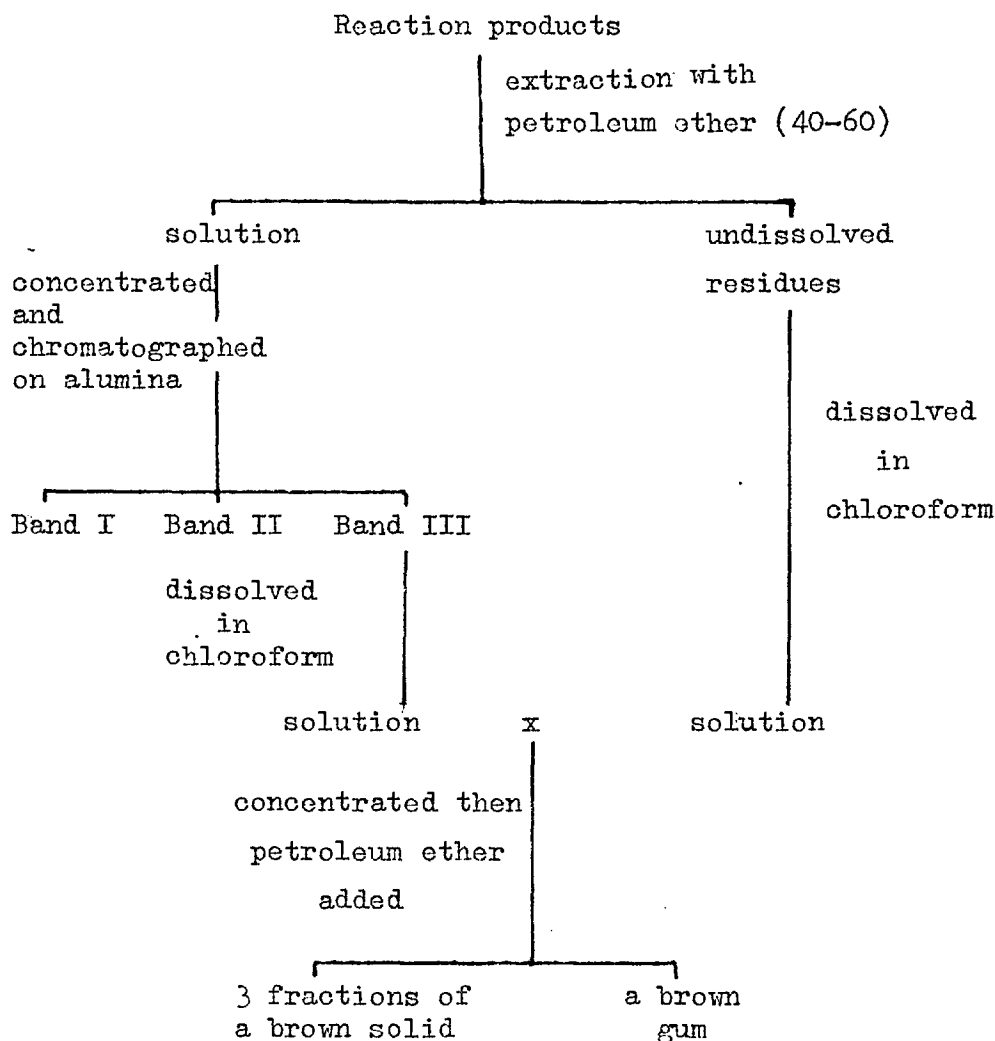
chromatographed on a 90 cm. column of D-lactose monohydrate in a 1:1 mixture of benzene and petroleum ether (b.p. 80-100). After seven hours the compound was collected in six fractions. The fractions were all identical and so it can be assumed that the compound was optically pure.

Trisacetylacetonatorrhodium(III):-

This yellow-brown crystalline solid was prepared by the method of Dwyer⁽⁹⁷⁾. m.p. 265°. The visible spectrum showed an absorption maximum at 320 mμ. $\epsilon = 9,630$.

Tris(+)-formylcamphorrrhodium(III) complexes.

The method of preparation was similar to that used for the preparation of trisacetylacetonatorrhodium(III). Rhodium(III) chloride trihydrate dissolved in water, was refluxed overnight with (+)hydroxymethylenecamphor dissolved in benzene in the ratio of one equivalent metal salt to three equivalents of the ligand. If alcohol is used as a solvent for the reaction, the (+)hydroxymethylene-camphor will reduce the rhodium(III) salt to rhodium(II) acetate if there is any acetate present. The aqueous solution was adjusted to pH.4. with sodium bicarbonate. The reaction went completely although some rhodium metal was deposited. The benzene layer was separated from the aqueous layer and was then evaporated to dryness. The separation of the reaction products is described in the scheme below:



Bands I and II passed through the column and gave yellow crystalline solids. Band III adhered to the top of the column and had to be eluted with chloroform.

(-)^{Tris}(+)^{formylcamphor}rhodium(III):-

This yellow crystalline solid was obtained by recrystallising the solid from Band I in ligroin three times. The specific

rotations of the three crops were: $[\alpha]_{370} = -20,700^{\circ}$, $-21,500^{\circ}$ and $-21,800^{\circ}$. The initial compound was therefore almost optically pure. The compound decomposed at 264° . The chromatography of this compound on D lactose monohydrate by the method which was used for the cobalt(III) compound did not produce any fractionation of the material. (Found: C, 62.38; H, 7.08; $\text{RhC}_{33}\text{H}_{45}\text{O}_6$ requires: C, 61.87; H, 7.03%.) The visible spectrum showed an absorption maximum at 343 mu. $\epsilon = 9,400$. The specific rotations in chloroform are $[\alpha]_{\text{D}} = -463^{\circ}$ and $[\alpha]_{370} = -21,800^{\circ}$.

Band II. Fraction:-

This yellow crystalline material was recrystallised from light petroleum. The visible spectrum in chloroform showed an absorption maximum at 343 mu. $\epsilon = 9,400$. The specific rotations in chloroform were: $[\alpha]_{\text{D}} = +77^{\circ}$ and $[\alpha]_{370} = -1,430^{\circ}$. The material was then recrystallised from chloroform. The crystals obtained had the optical rotation of the $(-)\text{Rh}(+\text{formylcamphor})_3$ isomer. The chloroform soluble residue had a specific rotation; $[\alpha]_{370} = +4,870^{\circ}$. The O.R.D. curve being approximately the inverse of the optically pure isomer. The Band II fraction is therefore a mixture of $(-)\text{Rh}(+\text{formylcamphor})_3$ and possibly $(+)\text{Rh}(+\text{formylcamphor})_3$. This component has not been obtained optically pure.

Ligroin-insoluble solids.

These light brown solids obtained in small yields in three fractions have not yet been characterised completely. The material melted at 222-224°. The visible spectrum shows an absorption maximum at 343 mμ. $\epsilon = 5,800$. The specific rotations in chloroform are; $[\alpha]_D = +103^\circ$ and $[\alpha]_{370} = -872^\circ$. The infra-red spectrum has a band at 3200 cm^{-1} , which suggests the presence of co-ordinated water.

Solvent effects of $(-)\text{Co}(+\text{formylcamphor})_3$.

The solvents used were of the General Purpose Reagent Standard. The concentration of the solutions used was 0.0090 g. solute in 100 ml. solvent.

Equilibrations:

$(-)\text{Co}(+\text{formylcamphor})_3$:-

A small amount of this complex was refluxed in methanol with a tenth of its weight of activated charcoal. There was no change in the optical activity in ten minutes boiling but after twenty four hours the complex had been decomposed to cobalt(II) compounds and polymeric cobalt(III) compounds.

$(-)\text{Rh}(+\text{formylcamphor})_3$:-

This complex was treated with activated charcoal in the same way as the cobalt(III) compound. The optical activity had not changed after nine hours refluxing. The composition of the Band II fraction did not change on similar treatment.

SECTION IV

The optically active acids used were obtained commercially. The specific rotations at the Na_D line were checked and compared with the literature values.

N-Benzoyl-L-alanine:-

This was prepared by the method in the literature⁽¹⁹²⁾ and had the properties mentioned therein.

Acetatopentamminecobalt(III) nitrate:-

This red crystalline compound was prepared by the method in Inorganic Syntheses⁽¹²⁹⁾. The visible spectrum was very similar to that described in the literature⁽¹³¹⁾.

(+)Lactatopentamminecobalt(III) nitrate:-

A red crystalline solid obtained by evaporating two equivalents of L(+)lactic acid with one equivalent of $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{NO}_3$ at 45° . The crystals were collected and washed with ethanol and ether. (Found: C, 10.28; H, 5.52; N, 28.77; Calc. for $\text{CoC}_3\text{H}_{20}\text{N}_7\text{O}_9$: C, 10.08; H, 5.73; N, 28.08%.) The visible spectrum showed absorption maxima at 501 m μ . $\epsilon = 55$, and 350 m μ . $\epsilon = 47$. The infra-red spectrum showed C-O stretching frequencies at 1608 cm^{-1} and 1325 cm^{-1} . This is in very good agreement with the values obtained by Nakamoto and his co-workers for $[\text{Co}(\text{NH}_3)_5\text{acetate}](\text{ClO}_4)_2$ ⁽¹⁹³⁾.

(-)*Malatopentamminecobalt(III)* nitrate:-

This red deliquescent compound was prepared in the same way as the lactato-complex. It was, however, very deliquescent and could only be obtained in the solid state after lengthy trituration with absolute methanol and acetone. The visible spectrum showed absorption maxima at 501 mμ. and 349 mμ.

Amino-acidopentamminecobalt(III) complexes.

Attempts were made to prepare such complexes with L-alanine, L-proline and N-benzoyl-L-alanine in a manner similar to that used for the complexes with α-hydroxy-acids. Evaporation of the solution at temperatures above 50° caused decomposition of the complexes, which was detected by the evolution of ammonia. Evaporation in vacuo at room temperatures did not bring about the co-ordination of the amino-acid.

(-)*Alaninatotetramminecobalt(III)* sulphate:-

This dark red solid was prepared by the method of Shimura⁽¹⁴⁰⁾. Considerable decomposition occurred if the complex was heated above 50°. (Found: N, 22.83; Calc. for $\text{CoC}_3\text{H}_{18}\text{N}_5\text{O}_6\text{S}$: N, 22.51%.) The visible spectrum showed absorption maxima 487 mμ. $\xi = 60$ and 347 mμ. $\xi = 66$.

(-)*Histidinatotetramminecobalt(III)* chloride:-

This dark red solid was prepared by a modification of the method of Shimura⁽¹⁴⁰⁾. The sulphate was converted to the chloride

by the addition of barium chloride solution. The red hygroscopic solid was precipitated with alcohol several times from an aqueous solution. (Found: Cl, 19.83; $\text{CoC}_6\text{H}_{20}\text{N}_7\text{O}_2\text{Cl}_2$ requires: Cl, 20.18%.) The visible spectrum showed absorption maxima at 492 m μ , $\epsilon = 74$ and 340 m μ . $\epsilon = 217$.

(-)Leucinatotetramminecobalt(III) perchlorate:-

This red solid was prepared by the method of Shimura⁽¹⁴¹⁾. The visible spectrum, which showed absorption maxima at 493 m μ , $\epsilon = 85$ and 348 m μ , $\epsilon = 88$, agrees well with that reported by Shimura.

(+)Tartratotetramminecobalt(III) chloride hydrate:-

This red solid was prepared by the method of Kirschner⁽¹⁰⁴⁾. (Found: Cl, 11.41; Calc. for $\text{CoC}_4\text{H}_{19}\text{N}_4\text{O}_7\text{Cl}$: Cl, 10.80%.) The visible spectrum showed absorption maxima at 515 m μ , $\epsilon = 66$ and 355 m μ . $\epsilon = 65$.

trans-Dichlorobis(-)propylenediaminecobalt(III) bisaquohydrogen chloride:-

The preparation and properties of this compound are described in Section II.

trans-Dichlorobis(-)propylenediaminerhodium(III) chloride:-

This pale yellow crystalline solid was prepared by the method of Basolo and Anderson⁽¹⁹⁴⁾. However the product was considerably more soluble than the corresponding ethylenediamine complex. The compound was recrystallised several times from methanol but it was very difficult to separate it from the potassium chloride produced

in the reaction. Sodium hydroxide was therefore substituted for potassium hydroxide in the reaction and the product was recrystallised four times from methanol. (Found: Cl, 27.05; $C_6H_{20}N_4Cl_3Rh$ requires: Cl, 29.80%.) The visible spectrum showed an absorption maximum at 405 mμ. $\epsilon = 51$.

Bis(+)propylenediaminenickel(II) perchlorate trihydrate:-

The preparation and properties of this compound are described in Section II.

Bis(-)stilbenediaminenickel(II) perchlorate:-

The preparation and properties of this compound are described in Section II.

SECTION V

E.S.R. spectra were measured on a Varian E.P.R. Spectrometer (100 kc/s model). The electronic spectra were obtained on a Perkin-Elmer Ultracord spectrophotometer.

Reagents

0.15M. solutions of the following compounds were prepared: D-tartaric acid, L-tartaric acid, racemic tartaric acid, L-glutamic acid, racemic glutamic acid, L-malic acid, racemic malic acid, citric acid, (+)glucose, copper sulphate, vanadyl sulphate, uranyl nitrate and sodium hydroxide. The compounds were all of the "Analar" grade. The specific rotations at the Na_D line were measured and compared with the literature values. The commercial racemic tartaric acid

was found to be dextrorotatory. This compound was therefore prepared by adding the D-tartaric acid solution to the L-tartaric acid solution until there was zero rotation. The composition of the hydrated vanadyl sulphate was found by volumetric analysis⁽¹⁹⁰⁾.

Electronic spectra

Equal volumes (5 ml.) of the metal salt solution and the acid solution were mixed in a conical flask. Sodium hydroxide was added from a burette. The visible spectrum of the solution in the flask was measured between the additions of the alkali. A known volume of water was added to the copper(II) and the vanadyl solutions before the titration to reduce the absorbance. The volumes of water added were:-

Copper(II) solutions - 10 ml.

Vanadyl solutions - 10 ml. followed by a further 20 ml. after four equivalents (20 ml.) of alkali had been added.

Fehling's test experiments

•15M copper(II) sulphate solution (5 ml.) and •15M tartaric acid or citric acid solution (5 ml.) were mixed in a conical flask. A known volume of •15M sodium hydroxide was added and the solution was diluted to 40 ml. 5 ml. of the diluted solution was added to a •15 M solution of (+)glucose (5 ml.). This solution was warmed on a steam bath at 70° for 5 minutes and the colour of the precipitate, if any, was recorded.

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