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OPTICALLY ACTIVE COMPLEXES OF COBALT(III) WITH BRANCHED CHAIN TETRADENTATE LIGANDS

by

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1968

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ABSTRACT

OPTICALLY ACTIVE COMPLEXES OF COBALT (III) WITH
BRANCHED CHAIN TETRADENTATE LIGANDS

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Two specially designed branched tetradentate ligands with nonidentical arms, bis-β-aminoethyliminoacetic acid (bis-β-AEIA) and β-aminoethyliminodiacetic acid (β-AEID), were prepared and reacted with carbonatotetraamminecobalt(III) ion and two other monodentate ligands or one other bidentate ligand to form octahedral complexes.

Only one isomer of $[Co(en)(bis\text{-}\beta\text{-}AEIA)]^{+2}$ was obtained which proved to be cis in configuration by its nmr spectrum. Here the cis refer to the complex in which the two primary amine nitrogens of the tetradentate are adjacent to each other.

Complexes with the general formula $[Co(diamine)(\beta\text{-}AEID)]^{+}$, where the diamine is ethylenediamine (en), l-cyclohexanediamine (l-chxn) or l-propylenediamine (l-pn), exist as both trans and cis isomers in which the two acetate oxygens of the tetradentate are opposite or adjacent to each other. These isomers were separated by cation exchange columns. The trans and cis isomers of $[Co(en)(\beta\text{-}AEID)]^{+}$ are identified by visible and nmr spectra of these compounds. The trans and cis isomers of $[Co(l\text{-}chxn)(\beta\text{-}AEID)]^{+}$ and $[Co(l\text{-}pn)(\beta\text{-}AEID)]^{+}$ are identified by their visible spectra. The cis-$[Co(l\text{-}pn)(\beta\text{-}AEID)]^{+}$ is resolved into optically active isomers during the column separation of geometrical isomers.

The optical rotatory dispersion and the circular dichroism spectra of the trans- and cis-$[Co(l\text{-pn})(\beta\text{-AEID})]^+$ and $[Co(l\text{-chxn})(\beta\text{-AEID})]^+$ ions are explained. The Cotton effects in trans complexes may be explained on the basis of vincinal effect alone whereas in the resolved cis complexes the optical activity is due to configurational as well as vincinal effect.

To my mother

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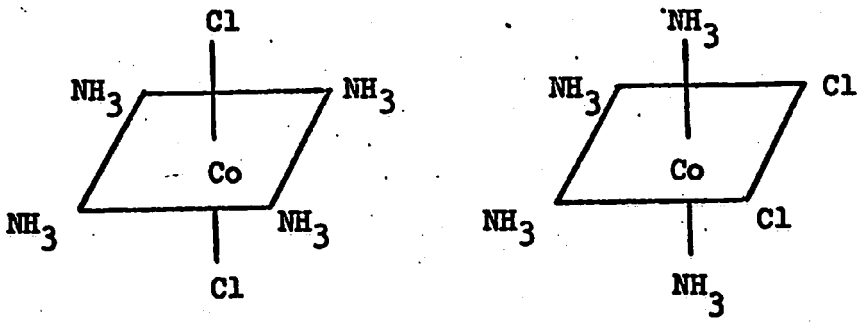
LIST OF ABBREVIATIONS

β-AEID	β-aminoethyliminodiacetate or β-aminoethyliminodiacetic acid
bis-β-AEIA	bis(β-aminoethyl)iminoacetate or bis(β-aminoethyl)iminoacetic acid
CD	circular dichroism
chxn	cyclohexanediamine
dien	diethylenetriamine
en	ethylenediamine
EDTA	ethylenediaminetetraacetate
IDA	iminodiacetate
IR	infrared
Mc	megacycle
MIDA	methyliminodiacetate
mu	millimicron
NTA	nitrilo triacetate
NMR	nuclear magnetic resonance
ORD	optical rotatory dispersion
ppm	parts per million
pn	propylenediamine
trien	triethylenetetramine
UV	ultraviolet
VE	calculated vincinal effect in cis-[Co(l-pn)(β-AEID)]$^{+}$ ion
VE'	vincinal effect in cis-[Co(l-chxn)(β-AEID)]$^{+}$ ion

I. INTRODUCTION

Stereoisomerism arises in chemical systems because molecules of the same composition may differ in arrangements of their atoms in space. For coordination compounds, the most common stereoisomers are the geometrical and optical isomers. There are many others such as positional isomers, linkage isomers etc., but they do not occur as often.

The geometrical isomers usually can be distinguished by using the terms cis and trans as in $[Co(NH_3)_4Cl_2]^+$ ion, the trans and cis isomers of this complex are shown in Figure I. Here the trans and cis refer to the relationships between the two chloride ions. The two chloride ions are opposite each other in trans and adjacent to each other in cis isomer.

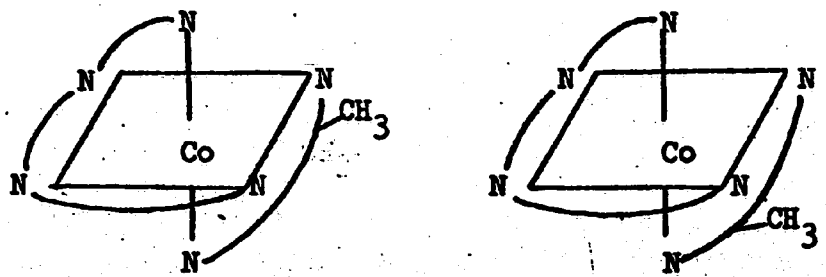


trans cis

Figure I. Trans- and cis-dichlorotetraammine cobalt (III) ions.

Optical isomerism exists in any molecules which do not have an improper axis Sn, where $n \geqslant 1$. Optical isomers can be devided into two types, namely enantiomers and diastereoisomers. The enantiomers are optical isomers which are non-superimposable mirror images of each other. The diastereoisomers are optical isomers which are neither mirror images of each other nor superimposable upon each other. They arise in coordination chemistry because the metal ion, which can be situated at a dissymmetric center, when surrounded by the various donor atoms and hence exist in two enantiomeric forms, can form a complex with one or more of the ligands which can also exist in two enantiomeric forms. For example in the complex β-triethylene-tetramine: (dl-propylenediamine)-cobalt (III) ion, β-[Co(dl-pn)(trien)]$^{+3}$ two configurational isomers D and L can exist for the complex, these, when combined with d and l propylenediamine, will form four possible diastereo-isomers, Dd, Dl, Ld, Ll. Here D and L are used to indicate the configurations of the octahedral complex, and d and l are used to indicate the configurations of the ligand propylenediamine.

Positional isomers arises due to the ways of orientation of an unsymmetrical ligand (usually a bidentate) when coordinated. For the β-[Co(dl-pn)(trien)]$^{+3}$ ion, the d- or l- pn in each of the diastereo-isomers can orient in two ways as shown in Figure II.



β-Form-1 β-Form-2

Figure II. Positional isomers of β-triethylenetetramine (propylenediamine) cobalt (III) ions
Lines replace the bridging atoms.

Linkage isomers differ in the actual atom of the donor molecule that is coordinated to the central atom. For example the NO_2 group in a complex with formula $[Co(NH_3)_5NO_2]^{+2}$ may be coordinated through oxygen or through nitrogen to form either a nitrito or a nitro isomer respectively.

The configuration refers to the actual positioning of all the atoms in a molecule relative to each other. For geometrical, positional, linkage and other isomers, configurations can often be determined without much difficulty, because difference in their physical properties or chemical reactivities. The determination of absolute configuration of optical isomers is particularly difficult because regular chemical or physical method as well as normal x-ray diffraction methods can not distinguish enantiomers from each other. (The diastereoisomers mentioned above in a sense are also enantiomers, if the configuration of the complex ion alone is considered.) A special x-ray technique, anomalous x-ray dispersion may be used to determine absolute configurations of enantiomers, but the measurement is slow and experimental conditions are fairly critical, only crystalline compounds in which a heavy atom is present as the anomalous scattering center can be measured. So far the absolute configurations of only a few complex ions have been determined by this method.

Chemical correlations which have been successfully used in correlating configurations for organic compounds by transforming one compound into another have not been too successful in complex compound because the complicated mechanisms involved. In general reactions of optically active complexes have not been well studied.

The most common methods which have been applied in relating configurations of optically active complexes are the less soluble diastereoisomers method, partial racemate method, stereospecific induction method and optical or spectroscopic method.

The less soluble diastereoisomer method has been used since the time of Werner (1). He proposed that complex ions have the same absolute configuration if they form the less soluble diastereoisomer with a given resolving agent. This was criticized later by Jaeger (2). He suggested that only isomorphous diastereoisomers should be used to compare configurations. However, sometimes it is difficult to define isomorphism. There are cases where both diastereoisomers are insoluble in certain solvents (3). Nevertheless for complexes which are isomorphous and the diastereoisomers are identical, this method can be used as a corroborative evidence in relating configurations.

Delépine (4) found that mixed one to one crystals of the potassium salts of $(+)_{546.1}$-$[Rh(C_2O_4)_3]^{-3}$ and (-)-$[Ir(C_2O_4)_3]^{-3}$ were of the same type as crystals of the racemate of either pure complex salt. He described this as "active racemate" formation, and attributed it to the opposite configurations of these two crystals. This has applied to other systems in determining optical configurations. Here again it is sometimes hard to say whether or not the crystals of the active racemate and the pure complex salt are of the same type.

The stereospecific induction method is based on a knowledge of the orientations of various groups in complex and the absolute configuration of the optically active ligand. As shown by Corey and Bailar (5) a coordinated ethylenediamine ring is puckered. Thus each ring can take one of two enantiomeric conformations in forming a complex. So in a complex like $[Co(en)_3]^{+3}$, besides the two configurational isomers it is possible to have four conformers for each configuration. For D-$[Co(en)_3]^{+3}$ complex in which the three ethylenediamine rings form a left handed spiral around the C_3 axis of this complex, the conformation of ethylenediamine ring which has its C-C

bond parallel to this C_3 axis of symmetry was defined as a k-ring whereas its enantiomer was defined as a k'-ring (5). For this complex the four possible arrangements of ethylenediamine rings are therefore kkk, kkk', kk'k' and k'k'k'. It was calculated that for D-$[Co(en)_3]^{+3}$, the kkk form is favored over the k'k'k' by an energy difference of 1.8 kcal/mole or 0.6 kcal/ring. So the kkk form exist predominantly in the equilibrium mixture. The most stable (D-(kkk)) was called lel while the least stable (D-(k'k'k')) was named ob. These results have been used by Corey and Bailar (5) to predict the configuration of D-$[Co(\underline{d}\text{-pn})_3]^{+3}$. When propylenediamine is coordinated to cobalt, the methyl group is in either an axial or equitorial position depending on the conformation of the ring. Calculations indicate that an equitorial CH_3 is favored over an axial CH_3 by approximately 2 kcal/mole. Thus in forming D-$[Co(\underline{d}\text{-pn})_3]^{+3}$, the methyl groups will all occupy the equitorial position. From the known absolute configuration of d-propylenediamine (6,7,8), it was found that to place CH_3 in equitorial position the d-propylenediamine must have k conformation. So the induced configuration was predicted to correspond to the configuration of D-$[Co(en)_3]^{+3}$. This was confirmed later by x-ray studies (9). This method of correlating configurations has been applied to predict the configurations of complexes of this type with optically active diamines other than d-pn and with central metal ions other than cobalt (10). It also predicted the right configuration for (+)-α-tris (L-alaninato)-cobalt (III) ion (11). However, the usefulness of this method is limited to systems where the energy difference between the different orientations of groups are known and fairly large.

The optical or spectroscopic method involves the measurement of optical rotatory dispersion (ORD) and circular dichroism (CD) spectra of optical isomers and relating these to the configuration. Since the measurement of ORD

and CD can be fairly easily done this method has attracted much attention lately. The successful use of this method provides a convenient means of correlating configurations of cationic, anionic as well as neutral species.

It is a well known fact that just as a pair of enantiomers are mirror images of each other so are their ORD and CD curves. The assignment of absolute configuration would be trivial if for a particular enantiomer, the sign of the Cotton effect associated with a particular transition could be calculated and hence its configuration determined. Although several models have been proposed as discussed by Woldbye (12), the theoreticians so far have not solved this problem for even the simplest optically active complex ion. At the present time the configuration of a dissymmetric complex ion is still determined by comparing the sign of the Cotton effect of certain transition with a related standard.

Since the discovery of Cotton effect (13,14), which is associated with certain transitions in optically active complexes, it has been applied to correlate configurations of cyclic organic carbonyl compounds. For a dissymmetric cyclic carbonyl compound, the enantiomeric stereochemical environments around the carbonyl chromophore will induce a Cotton effect of opposite signs to the magnetic dipole allowed carbonyl $n \rightarrow \pi^*$ transition at around 300 mμ (15). Since absolute configurations of a large number of dissymmetric cyclic carbonyl compounds are known, an octant rule (16) which defines the chirality or stereochemical environment around the carbonyl group has been proposed to correlate the absolute configurations of cyclic carbonyl compounds and the signs of Cotton effects at carbonyl $n \rightarrow \pi^*$ transitions. Knowing the sign of Cotton effect at $n \rightarrow \pi^*$ transition for a given cyclic carbonyl compound, it is possible to specify its configuration by this octant rule. So far for inorganic complex ions there exists yet no such generalized

octant rule. This is because of several difficulties which exist for optically active complex ions but do not exist in organic cyclic carbonyl compounds. Before describing what has been done and the problems involved in applying this spectroscopic method to dissymmetric complex ion, it is desirable to briefly review the nature of interaction of polarized light with optically active media.

The electric vector of plane polarized light can be thought of as composed of two circularly polarized components of equal amplitude which are rotating in the opposite directions at equal rates. Each component in its propagation direction is thus generating a helix of opposite handedness. When plane polarized light is passed through a medium containing dissymmetric molecules with a special chiral structure, a diastereoisomeric kind of interaction will exist for the two components of the plane polarized light. It is then not hard to imagine that the properties of the two components of a plane polarized light are affected to a different extent after passing through such a medium. As a matter of fact, the velocity or the refractive index for a left and a right handed circularly polarized light differs after passing through such a medium. This is called circular birefringence. Furthermore when the medium has an optically active absorption band, the molar extinction coefficients for the left and the right circularly polarized light are different when measured at the wavelength of that absorption band. This is called circular dichroism. These two phenomena combined together constitute the Cotton effect. The difference in velocity of the two components of the plane polarized light results in change of plane of polarization or rotation of the light. The change of velocity and molar extinction coefficient simultaneously result in elliptically polarized light. Both rotations and the difference between molar

extinction coefficients for right, ϵ_r and left, ϵ_l circularly polarized light are wavelength dependent. A curve of rotation versus wavelength is called an optical rotatory dispersion (ORD) curve whereas a curve of $\epsilon_l - \epsilon_r$ versus wavelength is called a circular dichroism (CD) curve. If in the region of optically active absorption band the ORD changes rapidly from a positive peak to a negative trough on changing from longer to shorter wavelength, the compound is said to have a positive Cotton effect at that transition and the CD curve will exhibit a positive peak at that absorption band. The mirror image effects are called negative Cotton effects. The CD curve which is either positive or negative and has a gaussian shape is much more easily resolved than an ORD curve which has both a peak and a trough as well as a non-zero magnitude even far away from an optically active transition. The mirror image relationship between ORD and CD curves of a pair of enantiomers are especially noticeable near an optically active transition.

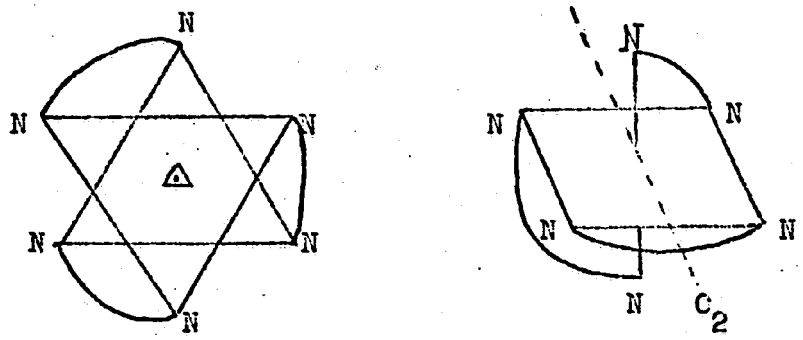
There are three reasons that the transition metal ions such as Co(III), Cr(III), Rh(III), Ir(IV) and Pt(IV) are chosen for optical activity studies. First of all these metal ions form kinetically inert complexes. Hence the resolutions of optical isomers are possible and the rates of racemization are slow. Of all the resolved complexes, those of octahedral cobalt (III) are the most numerous. Secondly, the electronic transitions of these complexes which are essential for the study of optical activity are reasonably well understood. Thirdly, the optically active transitions of dissymmetric complexes formed by these metal ions occur in the spectral region which is at the present time experimentally accessible.

In relating the Cotton effect to optical configurations of complex ions, the difficulties are unlike those for optically active cyclic carbonyl compounds. There are not as many different types of dissymmetric metal

complex ions available and even fewer of them whose absolute configurations have been determined by x-ray methods. So far the most thoroughly studied dissymmetric complexes are either the tris-bidentate type or the cis-bis-bidentate type. Too, the d-d transitions of transition metal ions are much more complicated than carbonyl $n \rightarrow \pi^*$ transition. Since the symmetry of this type of complexes is always lower than cubic, the excited states of optically active transition in dissymmetric complex ions split into at least two levels and hence the Cotton effect associated with the transition is split into at least two components. It is necessary, therefore, to identify at least one of the components in order to relate absolute configurations of two complexes on the basis of Cotton effect. At present few of these optically active transitions of dissymmetric complexes have been assigned with certainty. Again, there is sometimes a vincinal effect to be considered. (Vincinal effect refers to the optical activity induced by coordinated optically active ligand.)

In relating absolute configurations, (+)-tris(ethylenediamine)cobalt (III) ion will be used as an example to illustrate the method, since this is the most thoroughly studied complex in this respect.

The configuration of (+)-$[Co(en)_3]^{+3}$ as determined by x-ray (17,18,19) is shown in two different projections in Figure III. In this complex an



(a) (b)

Figure III. Configuration of (+)-tris(ethylenediamine)-cobalt (III) ion. Lines replace the bridging atoms.

obvious helix is formed by the three bidentate rings as shown in the figure. The symbols D and L have been used by early workers, and $\Lambda(C_3)$ and $\Delta(C_3)$ have been proposed by Piper (20) and also $\Delta(C_2)$ and $\Lambda(C_2)$ have been used by Legg and Douglas (21) to define the different chiralities or configurations. The complex shown in Figure III is D, $\Lambda(C_3)$ or $\Delta(C_2)$ in configuration according to the above terminology and its enantiomer is L, $\Delta(C_3)$ or $\Lambda(C_2)$ in configuration. If viewed along its C_3 axis (see Figure III (a)) this complex ion is a left handed propeller and if viewed along any of its C_2 axis as shown in Figure III (b), it is a right handed propeller. Hence in another paper by McCaffery et al. (22) this complex ion was denoted as $M(C_3)P(C_2)$ where M means minus and P means plus. Bis-bidentate complexes and certain multidentate complexes that also have C_2 axes can be related in configurations via C_2 axis chirality.

For octahedral (O_h) cobalt (III) complexes in a strong ligand field there are two absorption bands in the visible and near UV region, the longer wavelength band, corresponding to the $^1A_{1g} \longrightarrow {}^1T_{1g}$ transition, is magnetic dipole allowed and hence optically active. The shorter wavelength band is magnetic dipole forbidden and hence optically inactive. However because of symmetry effects this band will mix with the longer wavelength absorption band and acquire a small amount of optical activity. The $^1A_{1g} \longrightarrow {}^1T_{1g}$ transition has been chosen for relating the absolute configuration to the sign of Cotton effect in Cobalt (III) complexes (23). In optically active cobalt (III) complexes this band will split into two or three components depending on the symmetry of the complexes. The symmetry of $[Co(en)_3]^{+3}$ is lowered from O_h to D_3 and the first absorption band is split into two bands corresponding to $^1A_1 \longrightarrow {}^1E_a$ and $^1A_1 \longrightarrow {}^1A_2$ transitions. The splitting does not show in the electronic absorption spectrum but is observed in its

CD spectrum. In the CD spectrum of $[Co(en)_3]^{+3}$ the two bands corresponding to these transitions are of the opposite sign suggesting that the absorptions that are involved are of the opposite chirality (22). Therefore, in using Cotton effects to compare the absolute configurations in this type of complexes, it is necessary to identify at least one of these two energy levels and relate it to a particular chirality. In this complex ion it is the ^1E_a transition which must be assigned (24).

In assigning the transition associated with configuration, the prediction made by Piper (25) on the relative positions and signs of Cotton effects for ^1E_a and $^1A_1$ were proved later to be wrong (26). McCaffery et al. (26) used polarized light propagated along C_3 axis of D-(+)-$[Co(en)_3]^{+3}$ ion in crystalline 2(+)-$[Co(en)_3]Cl_3 \cdot NaCl \cdot 6H_2O$ to assign the ^1E_a transition. Only the transition with E symmetry is allowed for light polarized in this fashion. The results show that $^1A_1 \longrightarrow {}^1E_a$ lie at lower energy than $^1A_1 \longrightarrow {}^1A_2$ and the former transition gives a positive Cotton effect. This band is also the major CD band in solution. It was postulated that for dihedral d^6 complexes if ^1E_a transition shows a positive Cotton effect the complexes have the D absolute configuration.

The Cotton effect induced by a coordinated optically active ligand was discovered by Pfeiffer (27). This effect was subsequently found by others in various metal complexes with various optically active ligands. The effects are generally very small in magnitude in comparison with the configurational effect and are especially small when the optically active ligand is monodentate (28). In the study of complexes of $[Co(NH_3)_4AA]^{+2}$ type where AA is an optically active amino acid, it was found by Dunlop et al. (29) that the amino acids of the same configuration induced Cotton effect of the same sign in a corresponding d-d transition. In the study

of (-)-trans-$[Co(-AA)_2Cl_2]^+$ and $[Cu(-AA)_2]^{+2}$ where AA is an optically active diamine by Gillard (30), the rationale that optical diamine of the same absolute configuration will induce Cotton effect of the same sign at corresponding d-d transition has been used and the configurations of many optically active diamines have been related. In this study for example (-)-pn has been shown to have the same configuration as (-)-chxn. In a study of $[Co(en)_2aa]I_2$, where aa is an optically active amino acid, and tris(alaninato)cobalt (III), it was found by Liu et al. (31) and by Douglas et al. (32) that the configurational and vincinal effects are additive. Further, in the study of tris(alaninato)cobalt (III) (32) and tris(l-propylenediamine) cobalt (III) by Douglas (33), the configurational and vincinal effects have been separated. It was found that the configurational effect contributed mostly to the ^1E_a transition and vincinal effect contributed mostly to the $^1A_2$ transition. As pointed by Legg et al. (34), "The vincinal effect includes any contribution from the asymmetric centers, the relative ring conformations and difference in interligand interactions. The relative importance of these contributions is expected to vary, although the chelate ring conformation is expected to be of greatest importance in most instances".

The origin of optical activity is not well understood. Although it is very likely that there are other factors which governs the optical activity of complexes, up to the present time the Cotton effect of a dissymmetric complex is invariably associated with the chiral arrangement of rings around the metal ion or the conformation of individual rings.

As mentioned before there is no generalized octant rule yet for inorganic complexes. An empirical "tentative octant rule" has been proposed by Harkins (35). He based his rule on a limited number of dissymmetric

complexes whose absolute configurations have been determined by x-ray analysis, stereospecificity, mechanism of reaction or diastereoisomer interrelationship. According to this rule, the absolute configurations of D- and L- tris(ethylenediamine) cobalt (III) and other complexes, whose optical activity is due either to the chiral arrangement of rings around metal ion, or to the conformation of individual rings, can be related in configuration by an octant sign (36). The octant sign is then correlated to the sign of Cotton effect of a particular d-d transition for a given complex, depends on the symmetry of the complex. The success of this kind of rule will make it possible to compare the sign of the Cotton effect in certain transition and determine the absolute configuration of the complex.

The octant sign of a complex ion is derived by positioning the complex in a right handed coordinate system so that the central atom is at the origin. The first chelate ring is placed so that the donor atoms lie in xy plane and have the coordinates (+x,+y) and (-x,+y). The octant sign of the ring atoms and any other rings is then determined. The sign of each octant is given by the sign of the ring atoms. The sign of the ring atoms is determined by products of its coordinates. The substituents on the chelate rings as well as any monodentate ligands are not considered, only positions of the ring atoms are thought to be important. For complex containing more than one set of rings or for multidentate complexes, all rings are individually so placed and the signs obtained for each position are added.

Recently Legg and Douglas proposed (21) a "ring pairing method" to define absolute configurations of complexes of various symmetry types. In this method all possible bidentate rings relative to a C_2 or pseudo C_2 axis are written down and designated as Δ or Λ in comparison with configuration of <u>cis</u>-[co en_2X_2]$^{+n}$. Here the $\Delta(C_2)$ configuration is equivalent to the

$\Lambda(C_3)$ or D configuration of $[Co(en)_3]^{+3}$ ion. Sets of adjacent rings and trans rings in the same plane are not counted because such pairs do not define a spiral pattern. The net chirality or the chirality which occurs the greatest number of times is said to determine the chirality of the complex and the optical activity of the complex.

In short, the octant rule considers only the position of ring atoms and the ring pairing method neglects the vincinal effect and counts only the net chiral set in defining the absolute configurations for complexes. The fact that they can be used currently in correlating the absolute configurations of a number of optically active complexes indicates that for these classes of compounds, the Cotton effect probably is primarily governed by the chiral arrangement of bidentate rings around metal ion or position of the ring atoms. However the limitation of these two rules are apparent. For example they do not define the chirality of an optically active octahedral complex containing six different monodentates. These rules will be undoubtedly tested further and revised as various types of new optical complexes are synthesized and as the factors govern the optical activity in complex ions are better understood.

II. STATEMENT OF PROBLEM

The origin of optical rotatory power in complexes is far from well understood. At the present time optical activity in complexes has been mainly associated with the spiral arrangement of bidentate rings around the metal ion or conformations of coordinated optically active ligand.

The purpose of the present work is to synthesize complexes of a special symmetry type in which the rings cancel one another so that essentially it is non-helical in nature. The optical rotatory behavior of these complexes are to be distinguished from that of the helical structure complexes.

III. EXPERIMENTAL

A. Preparation of Bis-(β- aminoethyl)iminoacetic Acid Trihydrobromide

1. Preparation of Bis-(β-phthaloylaminoethyl) imide

This compound was prepared by the method of Liu (37). Potassium phthalimide (21 g, 0.113 mole) prepared according to Salzberg and Supniewski (38) was placed in about 150 ml of dimethylformamide. The bis-(β-chloroethyl)amine hydrochloride (5 g, 0.028 mole) was added in small portions at room temperature. After completing the addition, the mixture was heated under gentle reflux for over three hours. Upon cooling about 300 ml of chloroform and 400 ml of water were added. The aqueous layer which separated was extracted three times with portions of chloroform. The combined chloroform layers were washed twice with 0.2 N potassium hydroxide solution and then with water. The organic layer was dried with sodium sulfate, filtered and evaporated to dryness on the steam bath. The solid residue was recrystallized from 95% ethanol. The melting point of the product was 183-185°C. The yield was 5.1 g, i.e. 50%. It was found that attempts to make larger batches of the compound by increasing the quantities of the reagents and varying the reaction time one obtained only products of poor quality and low yields.

2. Preparation of Bis-(β-phthaloylaminoethyl)iminoacetic Acid Ethyl Ester

To 3.63 g (10^{-2} mole) of bis-(β-phthaloylaminoethyl)imide in 35 ml of dimethylformamide was slowly added 1.84 g (1.1×10^{-2} mole) of

bromoethylacetate in 15 ml of dimethylformamide. The solution was then refluxed gently for eighteen hours, after which 30 ml of water and 30 ml of chloroform were added. The mixture was separated in a separatory funnel. The aqueous layer was extracted with chloroform twice, the combined chloroform layers were washed with water twice and reduced on a steam bath to a small volume. After cooling to room temperature and addition of a few drops of water, a sticky residue formed. This was washed with ether twice and recrystallized from hot ethanol-water. The solid obtained had m.p. 93-103°C. The solid was recrystallized from hot ethanol-water containing Norit. The fine needle-like crystals formed on cooling were filtered and washed with cold absolute ethanol, air dried, (m.p. 104-105.5°C). The product was recrystallized again from hot ethanol-water filtered and air dried, (m.p. 104.5-106.5°C). Anal. Calcd. for $C_{24}H_{23}N_3O_6$: C, 64.13; H, 5.16; N, 9.35. Found: C, 64.12; H, 5.14; N, 9.29.

3. Preparation of Bis-(β-aminoethyl)iminoacetic-Acid Trihydrobromide

To 4.49 g (10^{-2} mole) of the above ester was added 75 ml of HCl-H_2O (1:1 by volume) solution. The mixture was refluxed gently in a round bottom flask for four hours. The phthalic acid formed after cooling was removed. The solution was further concentrated to a small volume whereupon more phthalic acid formed which was filtered and washed with cold water. The filtrate was evaporated until an oily residue formed. Attempts to isolate this compound in chloride form failed. A crystalline compound was obtained by slowly recrystallizing the residue from hydrobromic acid and ethanol-water mixture. For analysis the above solid was

recrystallized again from a hot ethanol-water solution containing hydrobromic acid, the solid separated was filtered and air dried. Anal. Calcd. for $C_6H_{18}N_3O_2Br_3$: C, 17.84; H, 4.49; N, 10.40; Br, 59.34. Found: C, 17.64; H, 4.59; N, 10.21; Br, 59.36.

B. Preparation of Bis-β-aminoethyliminoacetato (chloroaquo)or (diaquo) cobalt (III) Chloride

To a mixture of bis-(β-aminoethyl)iminoacetic acid trihydrobromide, bis-β-AEIA·3HBr (0.8080 g, 2 x 10^{-3} mole) and lithium hydroxide monohydrate (0.3360 g, 8 x 10^{-3} mole) in 10 ml of water was added carbonatotetraamminecobalt (III) nitrate· 1/2 H_2O (0.5152 g, 2 x 10^{-3} mole) in 10 ml of water. The mixture was diluted to 30 ml and heated on a steam bath for five hours or until all the ammonia had been driven off. The solution was filtered through Celite and evaporated under moving air to 5-10 ml, and several drops of conc. hydrochloric acid was added to it. The solution was concentrated further and ethanol was added to precipitate a lavender solid of $[Co(H_2O)_2(bis\text{-}\beta\text{-}AEIA)]Cl_2$. The solid was filtered and washed thoroughly with ethanol and air dried. Anal. Calcd. for $C_oC_6H_{18}N_3O_4Cl_2$: C, 22.10; H, 5.56; N, 12.89; Cl, 21.75. Found: C, 22.33; H, 5.62; N, 12.86; Cl, 21.59. When this solid was dissolved in water, the color of the solution changed from violet to red due to equation.

C. Preparation of Oxalato (bis-β-aminoethyliminoacetato)-cobalt (III)

A solution of carbonato (bis-β-aminoethyliminoacetato) cobalt (III) (2 x 10^{-3} mole) prepared as in B was filtered through Celite and

evaporated under moving air until a syrup formed. To the syrup was added 4 ml of water and the mixture was filtered to remove trace amounts of solid impurities. To the filtrate was added oxalic acid until the PH of the solution was about one. During this reaction bubbling of carbon dioxide was observed. The solution was evaporated on a steam bath to a few milliliters. After addition of ethanol to the hot aqueous solution to the oil point a red precipitate separated out on standing. Several fractions were obtained by repeating the above process. The main fraction was recrystallized from hot water. The dark red crystals of [Co(bis-β-AEIA)C_2O_4] were filtered and washed with cold water and air dried. Anal. Calcd. for [Co $C_8H_{14}N_3O_6$]: Co, 19.19; C, 31.28; H, 4.59; N, 13.68. Found: Co, 18.76; C, 31.10; H, 4.69; N, 13.55

D. Preparation of Cis-(bis-β-aminoethyliminoacetato)-(ethylenediamine) cobalt (III) Chloride

A solution of carbonato(bis-β-aminoethyliminoacetato)-cobalt (III) (4×10^{-3} mole) prepared as in B was filtered through Celite. To the filtrate was added ethylenediamine dihydrochloride (0.5321 g, 4×10^{-3} mole) and the mixture was heated on a steam bath for five hours. To the resulting solution was added sodium perchlorate (1.95 g, 16×10^{-3} mole) and the solution filtered. The colorless compound which separated upon standing was removed. Then an orange precipitate separated on further standing. This was filtered and washed with water and ethanol. Several fractions were obtained from the filtrate in this fashion. The fractions were combined and recrystallized from water twice. The orange-red crystalline compound so obtained was filtered and washed with water

and ethanol. For purification, this compound was dissolved in water and passed through a buret containing Dowex 50 W-X8 in chloride form at a rate of 0.5 ml/min. The chloride collected was evaporated to dryness, dissolved in minimum amount of water and precipitated from ethanol. The orange precipitate was filtered and washed with absolute alcohol, and air dried. Anal. Calcd. for $[CoC_8H_{22}N_5O_2]Cl_2$: C, 27.44; H, 6.33; N, 20.00; Cl, 20.25. Found: C, 27.55; H, 6.38; N, 19.90, Cl, 20.40.

E. Attempts to Separate and Resolve the Cis-(bis-β-aminoethylimino-acetato)(ethylenediamine) cobalt (III) Ion

1. Separation by Paper Chromatography

A concentrated solution of the complex ion was spread on a strip of Whatman chromatography paper and eluted overnight with 1-butanol-H_2O-HCl (60:30:10) mixture in a glass tank saturated with the vapor of the solvent mixture. Only one diffuse band was observed.

2. Separation on a Cation Exchange Cellulose Column

A concentrated solution of the complex ion was added to a buret packed with cation exchange cellulose, Cellex-CM (which has carboxymethyl exchange groups in Na form) in water. When the band was eluted with water and then with 0.01 N NaCl solution, only one broad band was observed.

3. Attempted Resolution with Optically Active Resolving Agents

a. Resolution with Ammonium-d-α-bromocamphor-π-sulfonate

The complex chloride (0.0875 g, 0.238×10^{-3} mole) and ammonium-d-α-bromocamphor-π-sulfonate (0.1560 g, 0.476×10^{-3} mole) were dissolved in 4 ml of hot water and allowed to cool to room temperature. The

diastereoisomers of the complex d-α-bromocamphor-π-sulfonate that crystallized out were filtered and washed with ethanol. From the filtrate, three more fractions were obtained this way. The ethanol washings were combined and evaporated to dryness. Compounds from all fractions had ORD curves similar to that of ammonium-d-α-bromocamphor-π-sulfonate. The recovered complex perchlorate obtained by adding sodium perchlorate to a concentrated solution of the diastereoisomer was optically inactive.

b. Attempted Resolution with Silver-d-α-bromocamphor-π-sulfonate

To a solution of silver nitrate (6.7956 g, 4×10^{-2} mole) in 10 ml of hot water was added ammonium-d-α-bromocamphor-π-sulfonate (13.1292 g, 4×10^{-2} mole) in 50 ml of water. The white needle-like crystals formed were filtered and washed with ethanol. More of the compound separated by concentrating the solution to a smaller volume. A total of 15-16 g was obtained. This was recrystallized from hot water and air dried. The yield was 11.5 g. To the complex chloride (3.5017 g, 10^{-2} mole) in 30 ml of water was added a suspension of silver-d-α-bromocamphor-π-sulfonate monohydrate (8.7221 g, 2×10^{-2} mole) in 30 ml of hot water. The solution was diluted to 250-300 ml and stirred for 15 minutes, then filtered from the silver chloride. The filtrate was evaporated until crystals started to separate. The crystals were redissolved completely by heating the mixture on a steam bath. Upon standing at room temperature, the diastereoisomer separated. Several fractions were obtained. All fractions had similar ORD curves to that of the resolving agent. The recovered complex perchlorate obtained by adding sodium perchlorate to a conc. solution of the diastereoismer was optically inactive.

4. Attempted Resolution of the Complex Ion by Stirring with d-quartz

Two grams of d-quartz powder was washed with dilute hydrochloric acid several times and then with water. To the complex ion (0.1530 g) in 15 ml of water was added 1 g of the above d-quartz and the solution stirred for 20 minutes. The solution was filtered and to the filtrate was added the remaining d-quartz and stirred for another 25 minutes. The quartz was removed by filtration and the filtrate was transferred to the cell. The ORD curve was taken between 600-350 mμ. The complex was optically inactive within experimental error.

5. Attempted Resolution of the Complex Ion with an Optically Active Complex Anion

To the complex chloride (0.240 g) in water was added l-K[CoEDTA] (0.503 g). The purple solution was filtered and the filtrate evaporated to dryness under moving air. The residue was recrystallized from ethanol-water. The purple crystals formed were filtered and washed with ethanol. They weighed 0.2810 g. From the red filtrate more purple needles crystallized out which were also filtered and washed with ethanol. The ORD and IR of the purple crystals indicate that the resolving agent was recovered.

F. Preparation of N-(β-phthaloylethyl)iminodiacetic Acid Diethylester

To dimethyliminodiacetate (9.45 g, 0.05 mole) in 450 ml of dimethylformamide was added β-bromoethylphthalimide (12.7 g, 0.05 mole). The mixture was then refluxed for nineteen hours. To the resulting

solution was added 300 ml of chloroform and 300 ml of water. The aqueous layer was extracted twice with chloroform. The combined chloroform layers were washed twice with water and evaporated on a steam bath until a syrup formed. To the syrup was added hot ethanol and water. After cooling to room temperature, the white precipitate which formed was filtered and washed with water. The yield was 5.5 g. This crude product was recrystallized from hot ethanol. The colorless crystals were filtered and washed with cold ethanol and air dried. The product weighed 4.2 g,-a 23% yield. The melting point was 94-97°C. Anal. Calcd. for $C_{18}H_{22}N_2O_6$: C, 59.63; H, 6.12; N, 7.73. Found: C, 59.89; H, 6.16; N, 7.50. All attempts to hydrolize this compound with hydrochloric acid to get the desired β-aminoethyliminodiacetic acid failed.

G. Preparation of β-Aminoethyliminodiacetic Acid Hydrosulfate

With slight modification, the procedure described by Schwarzenbach (39) was employed in preparing this ligand. Bromoacetic acid methylester (17.7 g, 0.116 mole) was added in portions to a mixture of N-carbethoxyethylenediamine (7.65 g, 0.058 mole)(prepared according to Rosenmund's method (40))and of potassium carbonate (8 g, 0.058 mole). After the initial heat evolution ceased, the slurry was heated on a steam bath for four hours. The paste formed was extracted with ether. The ether was later removed by evaporation on a steam bath. The oily residue was filtered from a trace amount of solid. The viscous yellowish N-carbethoxy-β-aminoethyliminodiacetic acid dimethyl ester thus obtained weighed 13.8 g. To 3 g of the above crude oil barium hydroxide octahydrate (9.47 g) in 200 ml of water was added. The mixture was heated on a steam bath for

two hours. After cooling 30 ml of 2N sulfuric acid was added and the barium sulfate precipitated was filtered through Celite. The filtrate was evaporated to dryness and recrystallized a few times from aqueous ethanol. The solid obtained was used in the following syntheses. Anal. Calcd. for $C_6H_{12}N_2O_4 \cdot H_2SO_4$: C, 26.27; H, 5.14; N, 10.22. Found: C, 25.49; H, 4.66; N, 9.92.

H. Preparation of β-Aminoethyliminodiacetato (diaquo) cobalt (III) Nitrate

To a mixture of β-aminoethyliminodiacetic acid hydrosulfate (0.5486 g, 2×10^{-3} mole) in 5 ml of water and barium hydroxide octahydrate (1.2620 g, 4×10^{-3} mole) in 5 ml of water was added carbonatotetraamminecobalt (III) nitrate-1/2 H_2O (0.5158 g, 2×10^{-3} mole) in 10 ml of water. The solution was heated on a steam bath for four and one half hours. The resulting solution was filtered to remove barium sulfate and other impurities. The filtrate was evaporated to dryness and dissolved in a small amount of water and a few drops of conc. perchloric acid was added in an attempt to make perchlorate of the complex. A violet red precipitate was obtained by adding ethanol to the above solution. The precipitate was filtered and washed with ethanol and redissolved in water. To this was added a few drops of conc. perchloric acid again and precipitated from ethanol. The precipitate so obtained was filtered and washed with ethanol and air dried. It was found by elemental analysis that the nitrate of the complex was obtained. Anal. Calcd. for $[CoC_6H_{14}N_2O_6] \cdot NO_3 \cdot 1/2\ H_2O$: C, 21.18; H, 4.44; N, 12.35, Cl, 0.00. Found: C, 21.54; H, 4.35; N, 11.99; Cl, 2.08, 2.12.

I. Preparation and Separation of the Isomers of β-Aminoethyliminodiacetato (ethylenediamine) cobalt (III) Ions

β-Aminoethyliminodiacetic acid hydrosulfate (2.1944 g, 8 x 10^{-3} mole) in 20 ml of water was mixed with barium hydroxide octahydrate (5.0480 g, 16 x 10^{-3} mole) in 20 ml of water. To the mixture was added carbonatotetraamminecobalt (III) sulfate trihydrate (2.0958 g, 4 x 10^{-3} mole) prepared according to Schlessinger (41) in 40 ml of water. The above mixture was diluted with 30 ml of water and heated on a steam bath for twenty three hours. The resulting mixture was assumed to contain 8 x 10^{-3} mole of carbonato (β-aminoethyliminodiacetato) cobalt (III) ion. The mixture was filtered from barium sulfate precipitate. To the filtrate was added ethylenediamine dihydrochloride. (1.0642 g, 8 x 10^{-3} mole) and heated on a steam bath for ten hours. The resulting dark red solution (25 ml) was added at a rate of 1 ml/min to a column (diameter 5 cm, length 60 cm) containing about 400 ml of Dowex 50 W-X8 cation exchange resin (50-100 mesh) in the sodium form. The complex formed an uneven red band at the top of the column. Water was then passed through the column at a rate of 2-3 ml/min until the eluent was colorless. Then the column was eluted with 0.5 N sodium perchlorate solution at 1.8 ml/min. Two red bands and one brown band separated on elution. The large first red band and the small second red band were collected in fractions while the top brown band moved very little. The fractions of the first red band identified by nmr to be the trans isomer were combined and evaporated to a small volume. The red precipitate which separated during the evaporating process was filtered and washed with ethanol. The product weighed 0.4860 g. Anal. Calcd. for trans-$[CoC_8H_{18}N_4O_4]ClO_4$: C, 24.47; H, 4.62; N, 14.26; Cl, 9.03. Found: C, 24.42; H, 4.65; N, 14.18; Cl, 8.97.

The above trans perchlorate (0.300 g) was dissolved in water and added to a Dowex 2-X8 anion exchange column in chloride form at 1.5 ml/min. The eluent was evaporated almost to dryness and precipitated from ethanol, air dried. Yield: 0.2750 g. Anal. Calcd. for trans-$[CoC_8H_{18}N_4O_4]Cl \cdot 3H_2O$: C, 25.11; H, 6.32; N, 14.64. Found: C, 25.06; H, 6.23; N. 14.76.

The fractions of the second band were combined and evaporated under moving air to a small volume. Large amounts of sodium perchlorate separated out. The sodium perchlorate was filtered and washed with ethanol. This process was repeated several times and finally the filtrate was evaporated to dryness. Ethanol was added to extract the sodium perchlorate and the ethanol insoluble complex was collected. The complex obtained was recrystallized from water and washed with ethanol. The red needles of the complex perchlorate weighed 0.1090 g. This isomer was dissolved in water and passed through a Dowex 2-X8 anion exchange column in Cl^- form and the solution evaporated to dryness. The residue was dissolved in minimum amount of water and precipitated from ethanol, filtered and washed with ethanol, and air dried. The nmr spectrum indicated that it was the cis complex. Anal. Calcd. for cis-$[CoC_8H_{18}N_4O_4] \cdot Cl \cdot 2H_2O$: C, 26.35; H, 6.08; N, 15.35. Found: C, 26.46; H, 6.09; N, 15.49.

J. Attempt to Resolve Cis-β-aminoethyliminodiacetato-(ethylenediamine) Cobalt (III) Chloride

Two grams of d-quartz were prepared as in E.4. One gram of this was stirred with 0.050 g of β-aminoethyliminodiacetato (ethylenediamine) cobalt (III) chloride in 10 ml of water for 15 minutes. The solution was filtered and to the filtrate was added the remaining d-quartz and

stirred for another 25 minutes. The solution was then filtered and an ORD curve of the solution was taken. It was optically inactive within experimental error.

K. Preparation, Separation and Purification of Isomers of β-Aminoethyliminodiacetato (1-cyclohexane-diamine) cobalt (III) Ions

To carbonate (β-aminoethyliminodiacetato) cobalt (III) ion (16×10^{-3} mole) prepared as in I. was added l-cyclohexanediamine dihydrochloride (2.98 g, 16×10^{-3} mole). The mixture was heated on a steam bath for twelve hours. Upon cooling the solid impurities were removed by filtration and washed with water. The combined filtrate was evaporated to dryness. Crystals formed during the evaporating process were redissolved in 20-30 ml of hot water. This solution was added to a cation ion exchange column (5 cm in diameter and 60 cm in length) containing Dowex 50 W-X8 (50-100 mesh) in the sodium form. The column was washed with water until the eluent was essentially colorless. Elution with 0.2N, 0.5N sodium perchlorate solution resulted in the separation of two red bands. The first band was collected in fractions and the ORD curves of all the fractions were found to be identical. These fractions were then combined and isolated by repeated removal of sodium perchlorate and addition of ethanol. Eventually, on addition of ethanol, a red solid precipitated. The solid was dissolved in water and filtered. The filtrate was evaporated to dryness and dissolved in minimum of water again. Upon addition of ethanol to this solution a precipitate separated. The precipitate was filtered and washed with ethanol, and air dried. Anal. Calc. for trans-$[CoC_{12}H_{24}N_4O_4]ClO_4 \cdot 2H_2O$: C, 29.85; H, 5.85; N, 11.61. Found: C, 30.09; H, 5.84; N, 11.72.

The second band was collected in fractions. The ORD curves for all fractions were taken. The peaks and troughs of the ORD curves for all fractions occur at essentially same wavelengths. However the peak at 500 mμ decreased in intensity gradually from the first to the last fraction. Due to the extremely low concentration of compound in all fractions, the fractions were combined, and isolated as for the cis isomer in I. The solid obtained weighed 0.035 g. Anal. Calcd. for cis-$[CoC_{12}H_{24}N_4O_4]ClO_4 \cdot NaClO_4 \cdot 1/2\ H_2O$: C, 24.93; H, 4.36; N, 9.69; Cl, 12.26; Na, 3.98. Found: C, 22.14; H, 4.06; N, 9.73; Cl, 16.66; Na, 33.81.

To purify the above cis compound a fresh iodide column was prepared as follows. A buret was packed with Dowex 2-X8 (50-100 mesh) in chloride form and 200-600 ml of 3 M sodium iodide solution was passed through the column. The column was then washed with 1-2l of water or until the test of iodide ion by silver nitrate solution was faint.

The cis isomer was dissolved in a minimum amount of water and passed through four of such freshly prepared iodide columns. Each time about 40 ml of eluent was collected. The eluent from the last column was evaporated to dryness, dissolved in a minimum amount of water and precipitated from ethanol. The precipitate was filtered and washed with ethanol, and air dried. It weighed 0.009 g. Anal. Calcd. for cis-$[CoC_{12}H_{24}N_4O_4]I$: I, 26.76. Found: I, 26.80.

L. Preparation, Separation and Purification of Isomers of β-Aminoethyliminodiacetato (1-propylenediamine)-cobalt (III) Ions

A solution of carbonato (β-aminoethyliminodiacetato)-cobalt (III) (8×10^{-2} mole) was prepared as in I. It was centrifuged and filtered through Celite. To the filtrate was added l-propylenediamine dihydrochloride

(11.7656 g, 8 x 10^{-2} mole). The mixture was heated on a steam bath for twenty-seven hours until the volume of the solution was reduced to 100 ml. This solution was filtered and the filtrate was added at a rate of 3 ml/min to a column (5.5 cm in diameter and 100 cm in length) packed with Dowex 50 W-X8 (100-200 mesh) cation exchange resin in the sodium form. An uneven band formed at the top of the column. The column was washed with water until the eluent was colorless, then it was eluted with 0.1N sodium perchlorate solution slowly. After the band had separated into two bands (trans and cis), the concentration of sodium perchlorate was increased to 0.2N. The trans band was collected in fractions.

The ORD curves were measured, the peaks and troughs of the ORD curves for all fractions occur at same wavelengths. The intensities of the peaks were normalized by assuming that the specific rotations at 675 mμ are constant for all fractions. The intensity of the peak at 475 mμ decreased slightly and gradually from the head to the tail fraction, while the intensity of the peak at 560 mμ remained essentially unchanged for all fractions. The head and tail fractions (T_1 and T_2) were isolated separately in the same fashion as for the trans isomers described in I and K. For analysis the solid isolated was dissolved in water, filtered. The filtrate was evaporated to a small volume and precipitated from ethanol. The precipitate was filtered and washed with ethanol and air dried. Anal. Calcd. for trans-T_1-$[CoC_9H_{20}N_4O_4]ClO_4$: C, 26.58; H, 4.96; N, 13.77. Found: C, 26.42; H, 4.91; N, 13.73. Anal. Calcd. for trans-T_2-$[CoC_9H_{20}N_4O_4]ClO_4 \cdot 1/2\ H_2O$: C, 26.00; H, 5.09; N, 13.48. Found: C, 26.28; H, 5.08; N, 13.50.

The trans-T_1 and trans-T_2 perchlorate were passed separately through two freshly packed Dowex 2-X8 anion exchange column in Cl^- form.

The solution collected was evaporated to dryness and washed with ethanol. Anal. Calcd. for trans-T_1-$[CoC_9H_{20}N_4O_4]Cl \cdot 1.5\ H_2O$: C, 29.24; H, 6.27; Cl, 9.59. Found: C, 29.02; H, 6.19; Cl, 9.82. Anal. Calcd. for trans-T_2-$[CoC_9H_{20}N_4O_4]Cl \cdot 1.5\ H_2O$ C, 29.24; H, 6.27; Cl, 9.59. Found: C, 29.13; H, 6.19; Cl, 9.80.

The concentration of the sodium perchlorate was eventually increased to 0.5N. The cis band eventually separated into two bands. The first cis band contained much more compound than the second one. The first cis band was collected in fractions and the ORD curves for all the fractions were measured. The fraction at very beginning of the first cis band had a peak at 460 mμ and a trough at 560 mμ. Then a fraction which had peaks at both 460 and 500 mμ, and a trough at 580 mμ was collected. This fraction was called $(+)_{500}$-cis-1. After this a fraction with peak at 500 mμ and trough at 580 mμ was collected. This fraction, which appeared to have the largest maximum rotation was named $(+)_{500}$-cis-2. A few other fractions with a peak at 500 mμ and a trough close to 600 mμ were obtained, their maximum rotations were considerably smaller. The concentration of these tested fractions were estimated by matching the color of the solution. The fractions $(+)_{500}$-cis-1 and $(+)_{500}$-cis-2 were isolated essentially in the same manner as the cis isomer in I. The compound isolated from the $(+)_{500}$-cis-1 fraction weighed 0.1980 g. Anal. Calcd. for $(+)_{500}$-cis-1-$[CoC_9H_{20}N_4O_4]ClO_4 \cdot 1.5NaClO_4 \cdot 1.5\ H_2O$: C, 17.52; H, 3.76; N, 9.09. Found: C, 17.49; H, 3.88; N, 9.09. After the isolation the ORD peak at 460 mμ for this fraction disappeared. For purification, $(+)_{500}$-cis-1 perchlorate was dissolved in water and passed through seven iodide columns prepared as in K, precipitated twice from ethanol, filtered and washed with ethanol and

air dried. The compound was slightly contaminated with sodium iodide. Anal. Calcd. for $(+)_{500}$-cis-1-$[CoC_9H_{20}N_4O_4]I \cdot 0.42\ NaI \cdot 1.8\ H_2O$: C, 20.42; H, 4.49; I, 34.03. Found: C, 20.44; H, 4.49; I, 33.98.

The compound isolated from fraction $(+)_{500}$-cis-2 weighed 0.228 g. Anal. Calcd. for $(+)_{500}$-cis-2-$[CoC_9H_{20}N_4O_4] \cdot ClO_4 \cdot NaClO_4 \cdot H_2O$: C, 19.76; H, 4.06; N, 10.24. Found: C, 19.80; H, 4.11; N, 10.34. For further purification the above $(+)_{500}$-cis-2 perchlorate was dissolved in water and passed through three freshly prepared iodide columns. The eluent was precipitated from ethanol, filtered and washed with ethanol, air dried. The yield was 0.095 g. Anal. Calcd. for $(+)_{500}$-cis-2-$[CoC_9H_{20}N_4O_4]I$: C, 24.90; H, 4.64; I, 29.24. Found: C, 24.71; H, 4.80; I, 29.10.

The second cis band was collected in fractions, since the ORD curves for all the fractions were essentially identical they were combined and called $(-)_{500}$-cis and isolated in the same manner as for cis isomer in I. The compound isolated weighed 0.2690 g. Anal. Calcd. for $(-)_{500}$-cis-$[CoC_9H_{20}N_4O_4]ClO_4 \cdot NaClO_4 \cdot H_2O$; C, 19.76; H, 4.06; N, 10.24; Cl, 12.97; Na, 4.2. Found: C, 19.82; H, 4.09; N, 9.60; Cl, 12.27; Na, 11.68. The above compound was dissolved in water and passed through two freshly prepared iodide columns and precipitated twice from ethanol filtered and washed with ethanol, and air dried. The yield of the purified product was 0.1220 g. Anal. Calcd. for $(-)_{500}$-cis-$[CoC_9H_{20}N_4O_4]I$: C, 24.90; H, 4.64; I, 29.24. Found: C, 24.69; H, 4.84; I, 29.40.

M. Visible Absorption Spectra

Spectra for optically inactive complexes were recorded at room temperature with a Cary Model 11 spectrophotometer using 10^{-2} M solution in 1 cm cells. Before obtaining the spectra, the instrument was adjusted

to give zero absorbance with water in the sample cell and with the reference cell empty. Spectra for optically active complexes were measured on a Jasco UV/ORD/CD-5 instrument.

N. Nuclear Magnetic Resonance Spectra

Spectra were recorded on a Varian A-60 spectrometer (60 Mc/sec) at about 35°. The spectrum of cis-β-aminoethyliminodiacetato(ethylenediamine) chloride was rerun on a Varian HA-100 (100 Mc/sec) to get better resolution. A reference standard of sodium -2, 2-dimethyl-2-silapentane-5-sulfonate (NaTMS) was used. All spectra were run in deuterium oxide with or without adding one drop of deuteriosulfuric acid to shift the HDO peak to lower field to facilitate the integration of the adjacent peaks. All resonances occurred to the low field side of NaTMS and were arbitrarily made positive.

O. Optical Rotatory Dispersion and Circular Dichroism Spectra

All the ORD curves of the tested fractions were measured over the range 6750 to 3500 Å on a Keston Model D Polarimeter attachment for a Beckman D.U. Spectrophotometer. The attachment was calibrated over the working range using freshly prepared sucrose solutions. The final spectra were obtained on a Jasco UV/ORD/CD-5 instrument at room temperature.

P. Infrared Spectra

Infrared spectra were obtained on a Perkin-Elmer Model 337 grating instrument using Nujol mulls.

Q. Analyses

All analyses were done by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

R. Reagents

Bis-(β-chloroethyl)amine hydrochloride was purchased from Hi Laboratories, Whitmore Lake, Michigan. Carbonatotetraammineçobalt(III) nitrate 1/2 H_2O, d-quartz and l-K[CoEDTA] were obtained from Dr. D. W. Cooke. Cation Exchange Cellulose Cellex-CM was purchased from Calbiochem Laboratories, Los Angeles, California. Ammonium-d-α-bromocamphor-π-sulfonate was purchased from the Aldrich Chemical Corporation. Potassium d-antimonyltartrate was purchased from General Chemical Co., New York. Diethyliminodiacetate was purchased from Eastman Organic Chemicals. l-Cyclohexanediamine dihydrochloride was obtained from Dr. Wade A. Freeman and l-propylenediamine dihydrochloride was obtained from Dr. Judith L. Doyle.

IV. RESULTS AND DISCUSSION

A. General

Complexes of various branched chain tetradentate ligands in which the chain is bifurcated at a donor atom such as $\beta\beta'\beta''$-triaminotriethylamine (42,43,44) and nitrilo triacetic acid (45,46) have been made and their stereochemistry studied. However chelates of this type with nonidentical arms have not been synthesized before.

Tetradentate ligands such as bis-(β-aminoethyl)-iminoacetic acid (bis-β-AEIA) and β-aminoethyliminodiacetic acid (β-AEID) are examples of ligands with nonidentical arms. When attached to a metal ion in an octahedral complex these ligands can form trans and cis geometrical isomers due to the stereochemical requirements of these ligands. For the bis-β-aminoethyliminoacetato (ethylenediamine)cobalt (III) ion, the isomer in which the two nitrogens of the tetradentate are opposite each other is denoted as the trans isomer (Figure IV (a)) whereas the isomer in which the two nitrogens of the tetradentate are adjacent to each other is denoted as the cis isomer (Figure IV (b)). For the β-aminoethyliminodiacetato(ethylenediamine)cobalt (III) ion, the isomer in which oxygens are opposite each other is denoted as trans (Figure IV (c)), while the isomer in which the two oxygens are adjacent to each other is denoted as cis (Figure IV (d)).

The 5th and 6th coordination sites which in the figure are occupied by ethylenediamine groups can be replaced by another bidentate or by two monodentates.

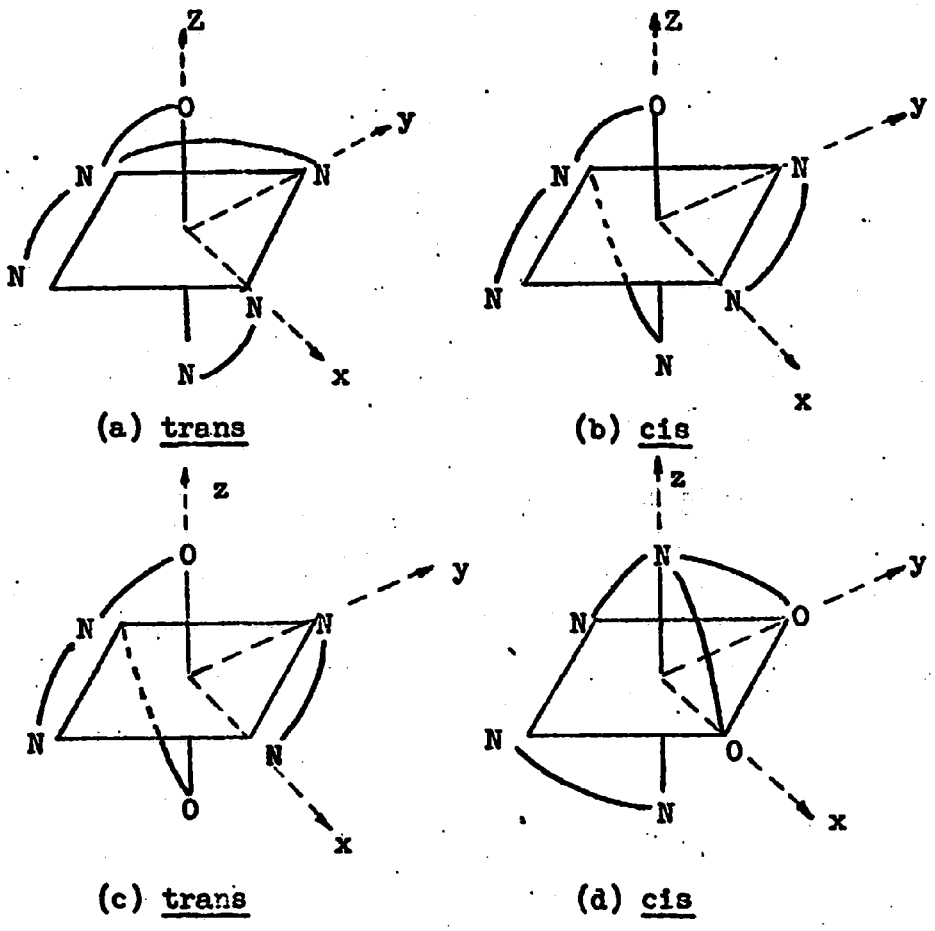


Figure IV. Geometrical isomers of bis-β-aminoethyliminoacetato (ethylenediamine)cobalt (III) ions (a), (b), and β-aminoethyliminodiacetato (ethylenediamine)cobalt (III) ions(c), (d). Lines replace the bridging atoms.

The cis isomers shown above will have optical isomers because of lack of an improper axis of rotation Sn. Yet according to the tentative octant rule (35), the resolved cis complexes shown in Figure IV (b) and IV (d) will have no octant sign (36) hence have zero optical activity; again, according to the ring pairing method (21) these cis complexes will have net zero chirality, hence no optical activity.

Stereochemical implications of the resolution of a cis complex with 5th and 6th positions occupied by two removable monodentates, are

evident. Because the possibility of a disproportionation reaction is minimized for complexes utilizing polydentate ligands, substitution reactions occuring at these 5th and 6th sites probably will not change the configuration of the complex.

In the present work, several octahedral cobalt (III), complexes of the tetradentate with one acetate group were made. They were the bis-β-aminoethyliminoacetato(chloro aquo) or (diaquo)cobalt (III) ion, the oxalato(bis-β-aminoethyliminoacetato)cobalt (III) and the Bis-β-aminoethyliminoacetato(ethylenediamine)cobalt (III) ion. The configuration of the $[Co(en)(Bis\text{-}\beta\text{-}AEIA)]^{+2}$ ion was found to be cis by its nmr spectrum. Several octahedral cobalt (III) complexes of the tetradentate with two acetate groups were also made. They were the β-aminoethyliminodiacetato(diaquo)cobalt (III) ion, the β-aminoethyliminodiacetato(ethylenediamino)cobalt (III) ion, the β-aminoethyliminodiacetato(l-cyclohexanediamine)cobalt (III) ion and the β-aminoethyliminodiacetato(l-propylinediamine)cobalt (III) ion. These compounds existed in both the trans and cis configuration. The geometrical isomers of the complexes of a diamine and the tetradentate were separated on cation ion exchange column. The configuration of trans- and cis-$[Co(en)(\beta\text{-}AEID)]^{+}$ were assigned by their visible and nmr spectra. The configuration of the trans and cis isomers of $[Co(l\text{-}chxn)(\beta\text{-}AEID)]^{+}$ and $[Co(l\text{-}pn)(\beta\text{-}AEID)]^{+}$ were assigned based on their visible spectra. The two cis isomers of $[Co(l\text{-}pn)(\beta\text{-}AEID)]^{+}$ which separated during the column elution were characterized by their ORD and CD spectra.

B. Preparation and Resolution of Isomers

In making these complexes it was found that the conventional method of oxidation of a cobaltous salt does not yield the desired products. The carbonatotetraamminecobalt (III) ion serves as a good starting material. Many unrelated complexes were made at the beginning just to test the feasibility of this method of preparation.

Attempted separation of geometrical isomers of [Co(en)(bis-β-AEIA)]$^{+2}$ ion by paper chromatography or on cation exchange cellulose column gave only one broad band which was identified as the cis isomer. Various methods were used to resolve this complex ion without success.

Geometrical isomers of [Co(diamine)(β-AEID)]$^{+}$ type complexes were separated by cation ion exchange chromatography. The two bands which came off the column have been assigned in order of their elution the trans and cis configurations for [Co(en)(β-AEID)]$^{+}$ ion on the basis of their visible absorption spectra and proton magnetic resonance spectra. All other complexes of this type were assigned configurations by comparing their visible spectra with that of the [Co(en)(β-AEID)]$^{+}$ ion. The order of elution for all other complexes of these series is also trans first followed by cis. This order of column elution agree with the observations of other investigators on trans and cis isomers containing monodentate ligands (47,48) and those containing multidentate ligands (49,50) of the $[CoN_4O_2]^{+}$ type. The trans and cis isomers have the same formal charge but the cis isomer has a greater effective dipole moment and hence is adsorbed more firmly on the column.

Because of the small amount of cis-[Co(en)(β-AEID)]$^{+}$ obtained from column separation in comparison with the corresponding trans, it was

difficult to carry out a resolution. Adsorption on d-quartz failed to resolve this cis complex ion.

Two diastereoisomers can exist for the cis-[Co(l-pn)(β-AEID)]$^{+}$, since cobalt (III) ion lies in the asymmetric center of this complex and is making use of an optically active ligand. Furthermore for each of the two diastereoisomers it is possible to have two positional isomers due to the two ways of orientation for the l-propylenediamine. For trans-[Co(l-pn)(β-AEID)]$^{+}$ ion only the formation of positional isomers are possible. The mechanism of separation of these optically active diastereoisomers on cation ion exchange column is not understood. But the fact that only cis-[Co(l-pn)(β-AEID)]$^{+}$ ion and not cis-[Co(l-chxn)-(β-AEID)]$^{+}$ ion is resolved on the column can be rationalized as follows: the different positioning of substituent CH_3 on the ring of coordinated l-pn has slightly changed the affinity of the diastereoisomers toward the resins.

C. Visible Absorption Spectra

1. Visible Spectrum of [Co(en)(bis-β-AEIA)]$^{+2}$ Ion

The visible spectrum of [Co(en)(bis-β-AEIA)]$^{+2}$ ion is shown in Figure V. The trans and cis forms of this complex both have effective $[CoN_5O]^{+2}$ or pseudo D_{4h} symmetry as can be seen from Figure IV (a) and IV (b). For this reason, the visible spectrum of this complex ion does not tell whether it is cis or trans in configuration. The crystal field theory will predict (51,52,53,54) for this complex ion a broadening of the band at the higher energy side of $^{1}A_{1g} \longrightarrow {}^{1}T_{1g}$ transition because in this ion the dipole moment in xy plane is greater than that along the Z direction

since nitrogen is higher in the spectrochemical series than oxygen. The absorption spectrum as shown in Figure V agree with this prediction, a slight broadening of the first band at higher energy side can be seen. The absorption peaks and molar extinction coefficients of this complex are summarized in Table I.

2. Visible Spectra of trans and cis-$[Co(diamine)(\beta\text{-AEID})]^+$ Ions

The visible spectra of trans and cis-isomers of $[Co(en)(\beta\text{-AEID})]^+$, $[Co(\underline{l}\text{-pn})(\beta\text{-AEID})]^+$ and $[Co(\underline{l}\text{-chxn})(\beta\text{-AEID})]^+$ are shown in Figure V, VI, and VII respectively. Both trans and cis complexes of this series have $[CoN_4O_2]^+$ or pseudo D_{4h} symmetry. Since N is higher in the spectrochemical series, according to crystal field theory (51,52,53,54) the trans isomer (Figure IV (c)) in which the dipole moment in xy plane is greater than that along the Z direction will split at the higher energy side of the first band, whereas the cis isomer in which the dipole moment in xy plane is smaller than that along the Z direction will have only a broadening of the first band at the lower energy side. This was observed for all the complexes in the β-AEID series. A summary of the absorption peaks is shown in Table I.

The absorption maxima for all of these complexes falls essentially at same energies. For the trans isomer the major first band occur at 1.9×10^4 cm^{-1} and a shoulder at $2.2\text{-}2.3 \times 10^4 cm^{-1}$. For the cis isomer the major peak occurs at $2.0 \times 10^4 cm^{-1}$ and a broadening at $1.8 \times 10^4 cm^{-1}$. All the maxima for the high energy absorption bands occur at 2.8×10^4 cm^{-1}. For the optically active $[Co(\underline{l}\text{-pn})(\beta\text{-AEID})]^+$ ions where more than one cis and trans forms were isolated, only representative curves for one trans

and one cis isomer are presented, (see Figure VI), although the maximum wavelength and molar extinction coefficients for all isomers isolated were shown in Table I.

The positions of the shoulders were obtained by subtracting a symmetrical trace of the first band from the original first band. The separations between the main peak of the first band and that of the parent compound (using the data for $[Co(en)_3]^{3}$ ion (49)) were calculated. The ratio of separation between trans and cis for [Co(diamine)(β-AEID)]$^{+}$ where diamine is ethylenediamine, l-propylenediamine and l-cyclohexanediamine respectively are 1.8, 1.9 and 2.0. These values agree quite well with the simple crystal field prediction for pure ionic monodentate complexes of this type (51). The only deviation from the theory is the intensity prediction. The prediction suggests that the cis isomer which does not possess a center of symmetry should have a more intense spectrum than the trans isomer which has this center of symmetry. The absorption spectra of all the trans isomers in this series have greater intensities than the corresponding cis isomers. This result however agrees with the spectra of a series of cobalt (III) complexes of IDA and MIDA made with dien by Legg and Cooke (50). As explained in their paper and by Ballhausen (55), in these d-d transitions the complexes gain intensity through the dissymmetry introduced by asymmetrical ligand vibrations. The vibrational motion in these chelate systems should be more complex than those of the monodentate complexes upon which the intensity predictions are based.

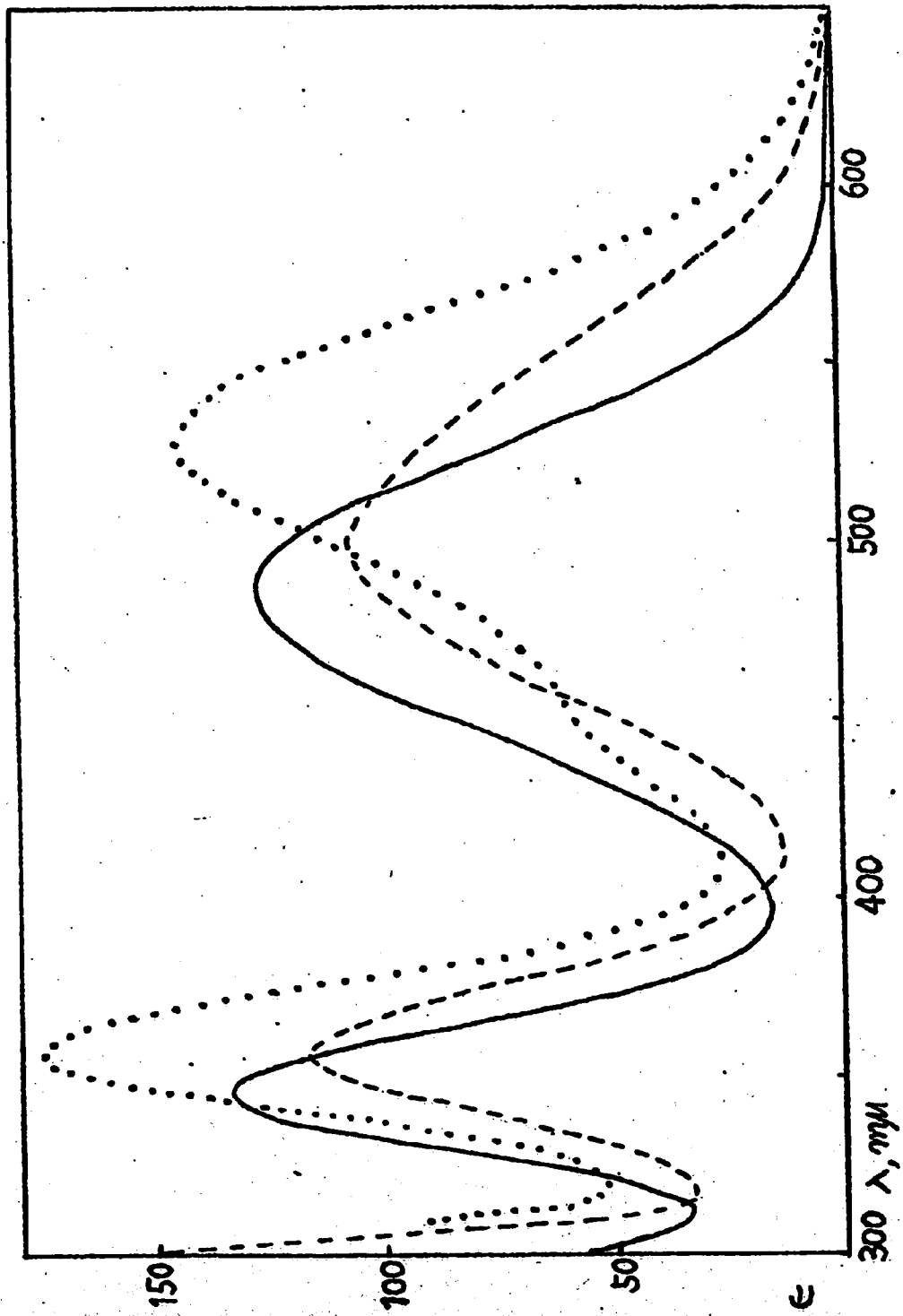


Figure V. Absorption spectra of cis-[Co(en)(bis-β-AEIA)]$^{+2}$, trans-[Co(en)(β-AEID)]$^{+}$ ····, and cis-[Co(en)(β-AEID)]$^{+}$ ----.

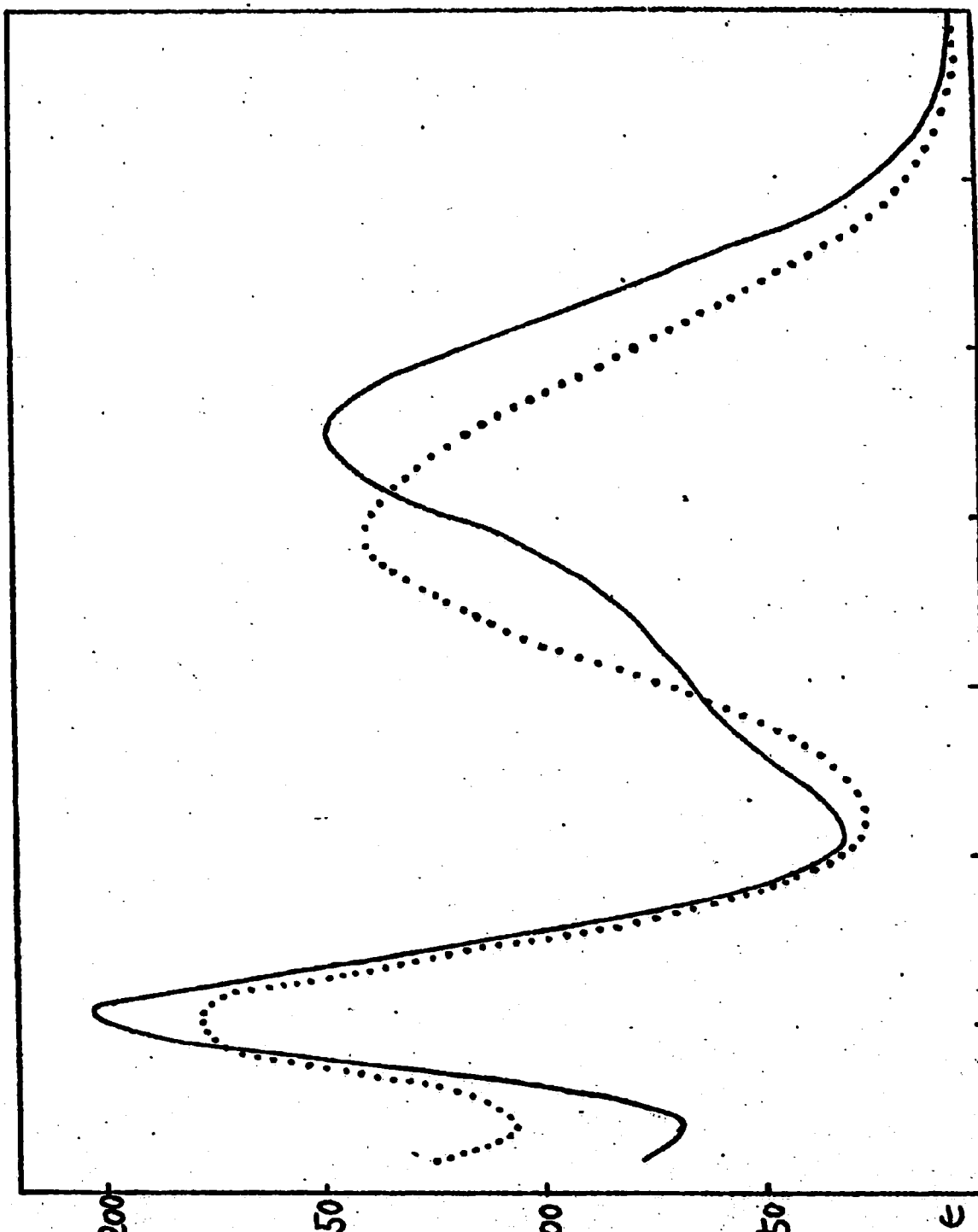


Figure VI. Absorption spectra of trans-T_1-[Co(l-pn)(β-AEID)]$^+$——, and (-)$_{500}$-cis-[Co(l-pn)(β-AEID)]$^+$.....

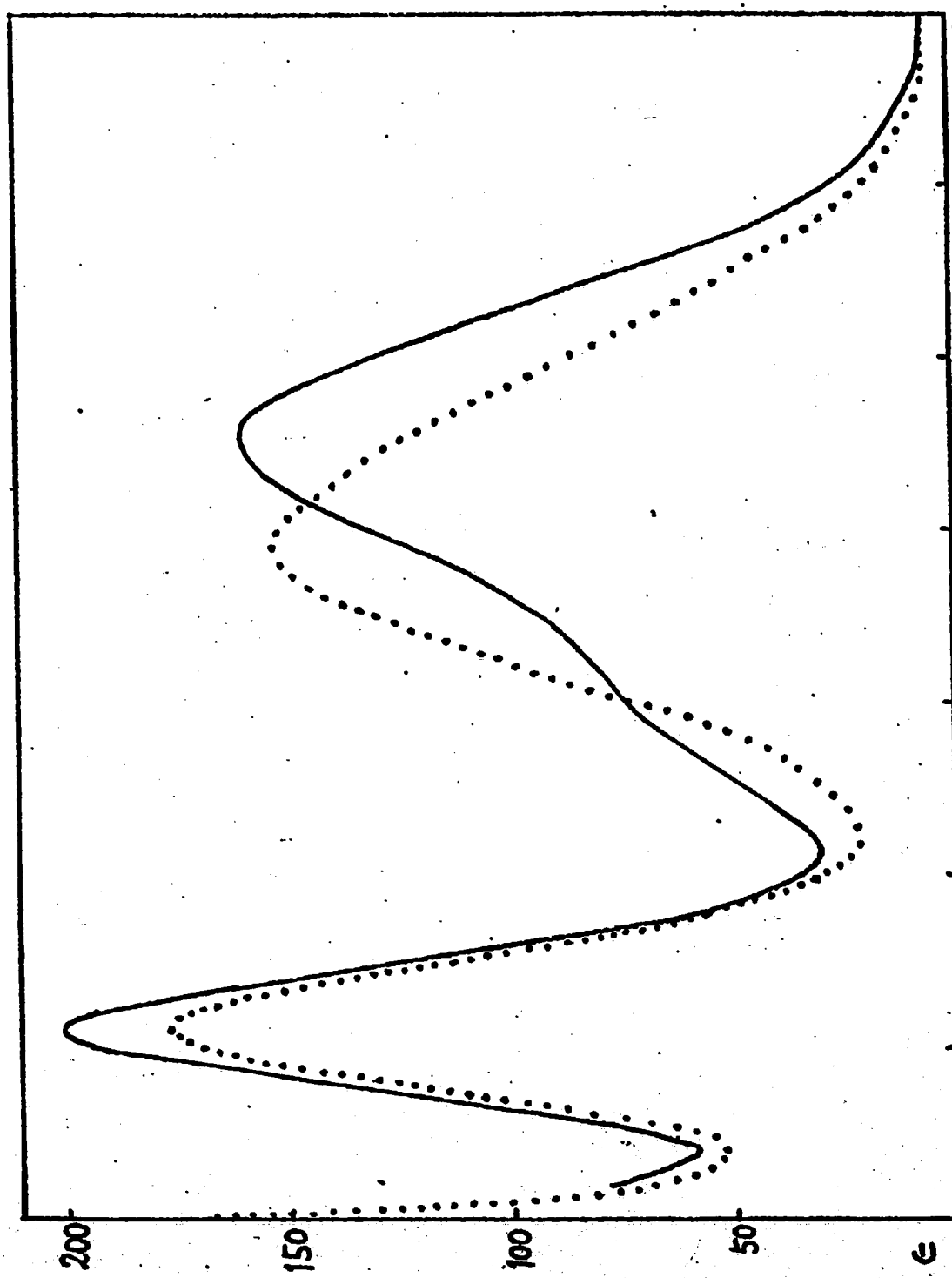


Figure VII. Absorption spectra of trans-[Co(l-chxn)(β-AEID)]$^+$ ——, and cis-[Co(l-chxn)(β-AEID)]$^+$ ····.

TABLE I

Absorption and Circular Dichroism of Complexes in $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ Spectral Region

Complex	Absorption (max. $\nu \times 10^{-4}$ cm^{-1})					
	I_a	(ϵ)	I_b	(ϵ)	II	(ϵ)
cis-[Co(en)(bis-β-AEIA)]$^{+2}$	2.06	(126.8)	-	(Sh)	2.89	(134.0)
cis-[Co(en)(β-AEID)]$^+$	1.79	(Sh)	2.01	(107.0)	2.80	(117.0)
trans-[Co(en)(β-AEID)]$^+$	1.90	(144.0)	2.24	(Sh)	2.80	(175.0)
$(-)_{500}$-[Co(l-pn)(β-AEID)]$^+$	1.81	(Sh)	2.02	(139.0)	2.84	(179.8)
$(+)_{500}$-cis-2-[Co(l-pn)(β-AEID)]$^+$	1.81	(Sh)	2.02	(139.9)	2.83	(172.5)
VE	-	-	-	-	-	-
$(-)_{500}$-cis-[Co(l-pn)(β-AEID)]$^+$-VE'	-	-	-	-	-	-
$(+)_{500}$-cis-2-[Co(l-pn)(β-AEID)]$^+$-VE'	-	-	-	-	-	-
$(+)_{500}$-cis-1-[Co(l-pn)(β-AEID)]$^+$	1.80	(Sh)	2.00	(118.0)	2.84	(181.6)
trans-T_1-[Co(l-pn)(β-AEID)]$^+$	1.91	(147.6)	2.27	(Sh)	2.82	(202.5)
trans-T_2-[Co(l-pn)(β-AEID)]$^+$	1.91	(174.4)	2.24	(Sh)	2.82	(221.2)
cis-[Co(l-chxn)(β-AEID)]$^+$	1.79	(Sh)	2.02	(152.7)	2.81	(177.0)
trans-[Co(l-chxn)(β-AEID)]$^+$	1.90	(159.8)	2.24	(Sh)	2.82	(201.2)

Complex	Circular Dichroism (extrema, $\nu \times 10^{-4}$ cm^{-1})					
	I_a	(ϵ)	I_b	(ϵ)	II	(ϵ)
cis-[Co(en)(bis-β-AEIA)]$^{+2}$	-	-	-	-	-	-
cis-[Co(en)(β-AEID)]$^+$	-	-	-	-	-	-
trans-[Co(en)(β-AEID)]$^+$	-	-	-	-	-	-
$(-)_{500}$-cis-[Co(l-pn)(β-AEID)]$^+$	1.85	(+1.45)	2.14	(-0.37)	2.88	(+0.18)
$(+)_{500}$-cis-2-[Co(l-pn)(β-AEID)]$^+$	1.86	(-1.21)	2.16	(+0.74)	2.84	(-0.40)
VE	1.84	(+0.12)	2.17	(+0.20)	2.84	(-0.11)
$(-)_{500}$-cis-[Co(l-pn)(β-AEID)]$^+$-VE'	1.85	(+1.30)	2.14	(-0.68)	2.84	(+0.25)
$(+)_{500}$-cis-2-[Co(l-pn)(β-AEID)]-VE'	1.85	(-1.37)	2.16	(+0.43)	2.82	(-0.30)
$(+)_{500}$-cis-1-[Co(l-pn)(β-AEID)]$^+$	-	-	-	-	-	-
trans-T_1-[Co(l-pn)(β-AEID)]$^+$	1.83	(-0.02)	2.23	(+0.13)	2.86	(-0.10)
trans-T_2-[Co(l-pn)(β-AEID)]$^+$	1.83	(+0.01)	2.22	(+0.13)	2.86	(-0.16)
cis-[Co(l-chxn)(β-AEID)]$^+$	1.86	(+0.15)	2.15	(+0.31)	2.74	(-0.09)
trans-[Co(l-chxn)(β-AEID)]$^+$	1.85	(+0.09)	2.21	(+0.18)	2.92	(-0.09)

VE is used to represent the calculated vincinal effects in cis-[Co(l-pn)(β-AEID)]$^+$ ion.

VE' is used to represent the estimated vincinal effects in cis-[Co(l-chxn)(β-AEID)]$^+$ ion.

D. Nuclear Magnetic Resonance Spectra

The proton magnetic resonance spectra were measured for [Co(en)(bis-β-AEIA)]$^{+2}$, and trans- and cis-[Co(en)(β-AEID)]$^{+}$ as shown in Figure VIII, IX, X and XI and summarized in Table II. Although there are three kinds of protons in these complexes, only the acetate and ethylene ring protons appeared in the proton magnetic resonance spectra of these complex ions. The amine protons apparently exchanged very rapidly with deuterium as these proton peaks were not observed.

1. NMR Spectrum for [Co(en)(bis-β-AEIA)]$^{+2}$ Ion

For complex with formula [Co(en)(bis-β-AEIA)]$^{+2}$, cis and trans isomers are possible (Figure IV (a) and (b)). In the cis isomer (Figure IV (b)) the orientation of the acetate ring places the two protons in different environment and an AB quartet is expected in the acetate ring protons region. For the trans isomer (Figure IV (a)) a singlet in the acetate ring protons region is predicted due to the equivalence of the two acetate protons. As shown in Figure VIII, in the acetate ring protons region, three peaks of the quartet appeared. The one at lower field is covered by HDO peak. The two peaks at higher field correspond to one of the two acetate ring protons integrated to 1.03 protons. The ethylene protons which appeared between 3.5 → 2.5 p.p.m. integrated to twelve protons. Hence this isomer was assigned the cis configuration.

2. NMR Spectra for [Co(en)(β-AEID)]$^{+}$ Ions

The complex with formula [Co(en)(β-AEID)]$^{+}$ identified by its visible spectrum as trans-[Co(en)(β-AEID)]$^{+}$ion exhibits the nmr spectrum

TABLE II

Resonance Frequency Assignments and Integration Values From the NMR Spectra of the Tetradentate Chelates

Assignment	cis-[Co(en)(bis-β-AEIA)]$^{+2}$		trans-[Co(en)(β-AEID)]$^{+}$		cis-[Co(en)(β-AEID)]$^{+}$	
	Res. Freq. p.p.m.	No. of H's	Res. Freq.	No. of H's	Res. Freq.	No. of H's
$-NH_2$	-	-	-	-	-	-
$-CH_2COO$	4.17 3.96 3.68	1.03	4.61 4.34 4.15 3.87	4.35	4.43 4.43 4.15 4.12 4.12 3.82 4.08 3.76	4.36
$\diagdown NCH_2CH_2N\diagup$	3.5 ↓ 2.50	12	3.57 ↓ 2.50	8.0	3.74 ↓ 2.34	7.94

in D_2O and D_2SO_4 shown in Figure IX. As expected one quartet integrated to 4.35 protons is found in the acetate ring protons region between 4.6 —>3.8 ppm due to the equivalence of the two acetate rings and the slightly different chemical environment for the two protons on each acetate ring in trans isomer (Figure IV (c)). The ethylene ring proton peaks appeared between 3.6 and 2.5 ppm integrated to 8.0 protons for this trans isomer, (Table II).

For the cis-$[Co(en)(\beta\text{-AEID})]^+$ isomer, the nmr spectrum as shown in Figure X integrated to 4.36 protons in the acetate ring protons region between 4.4 and 3.7 ppm (Table II). As shown in Figure XI, a better resolved spectrum obtained on a Varian 100 Mc nmr spectrometer clearly reveals two sets of quartets in this region as expected due to the slightly different chemical environment of the two acetate rings in the cis isomer. The en ring proton peaks appear between 3.7 and 2.3 ppm and give an integration of 7.9.

The chemical shifts calculated according to Jackman (56) for the acetate ring protons of the complexes are shown in Table III.

TABLE III

Chemical Shifts of Acetate Ring Protons of the Tetradentate Chelates

	δa	δb	$\delta a - \delta b$	$Jab/\Delta\nu ab$
cis-$[Co(en)(bis\text{-}\beta\text{-AEIA})]^{+2}$	4.27	3.86	0.41	0.69
trans-$[Co(en)(\beta\text{-AEID})]^+$	4.43	4.06	0.37	0.76
cis-$[Co(en)(\beta\text{-AEID})]^+$	δa^1	δb^1	$\delta a^1 - \delta b^1$	$Jab/\Delta\nu ab$
	4.05	4.21	0.16	1.09
	δa^2	δb^2	$\delta a^2 - \delta b^2$	$Jab/\Delta\nu ab$
	4.02	4.18	0.16	1.21

These values are consistent with the values obtained for $[Co(dien)(MIDA)]^+$ by Legg and Cooke (50) and [Co(en)(NTA)] by Cooke (57).

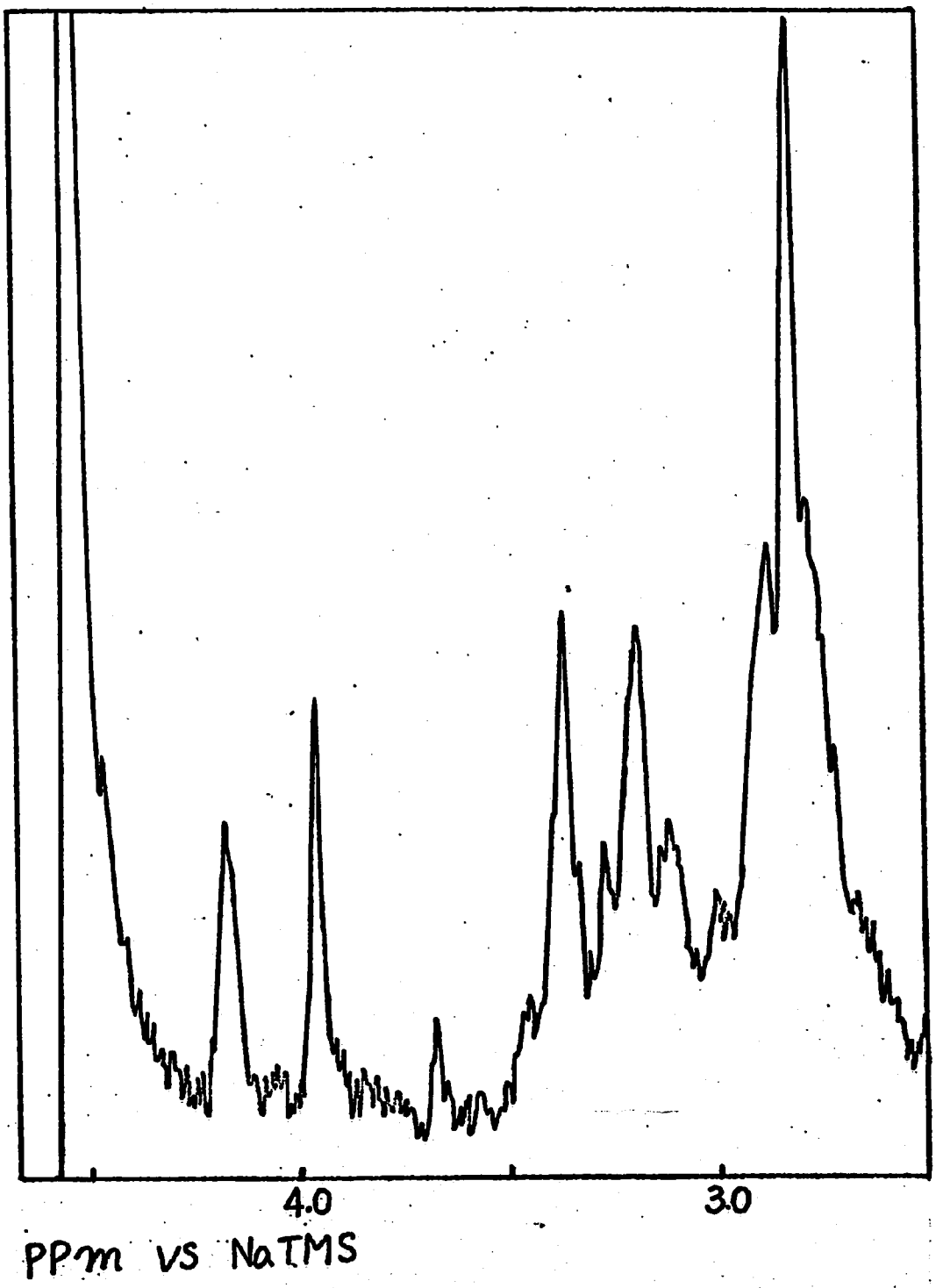


Figure VIII

Nmr spectrum of cis-[Co(en)(bis-β-(AEIA)]$^{+2}$.

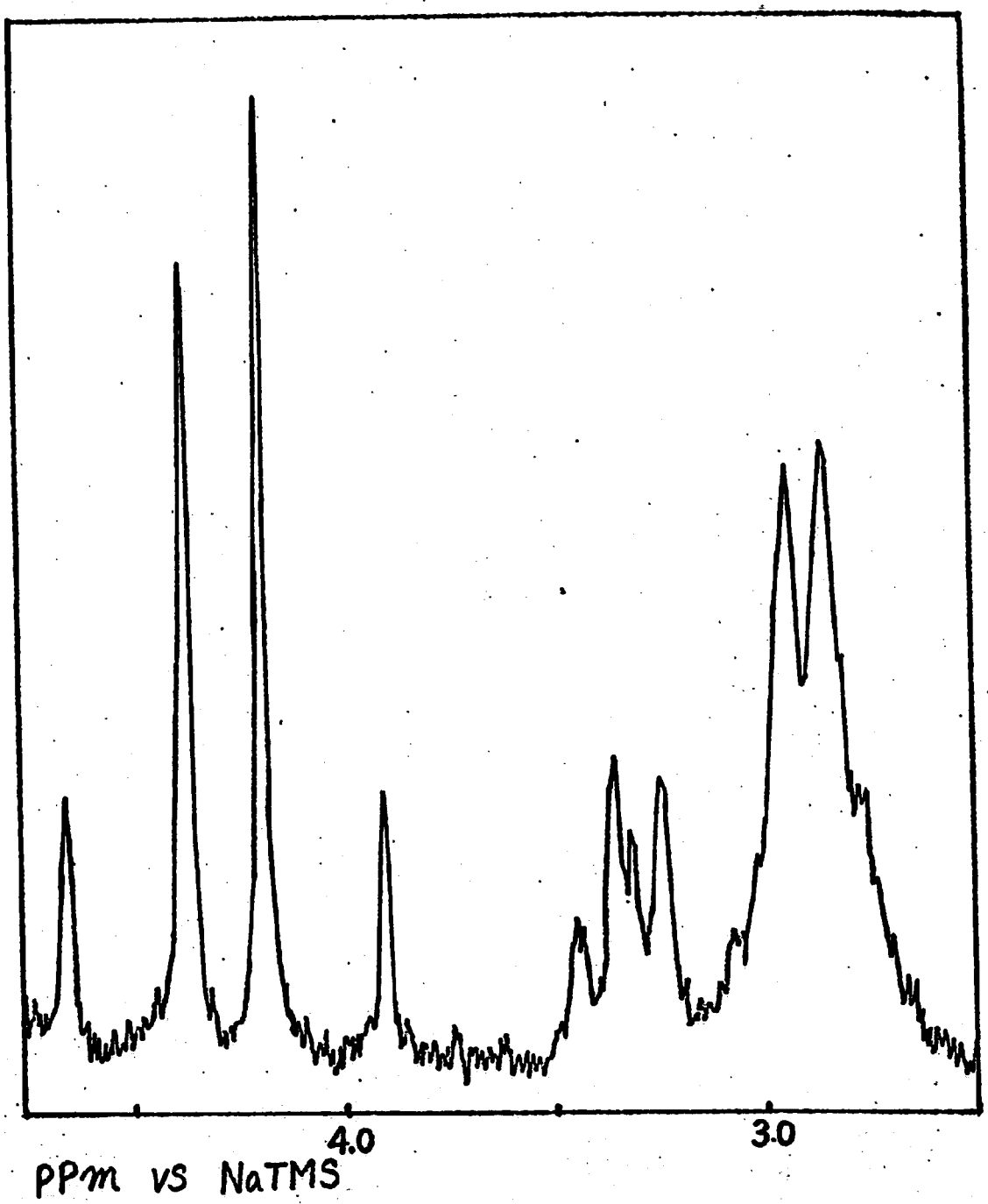


Figure IX

Nmr spectrum of <u>trans</u>-[Co(en)(β-AEID)]$^{+}$.

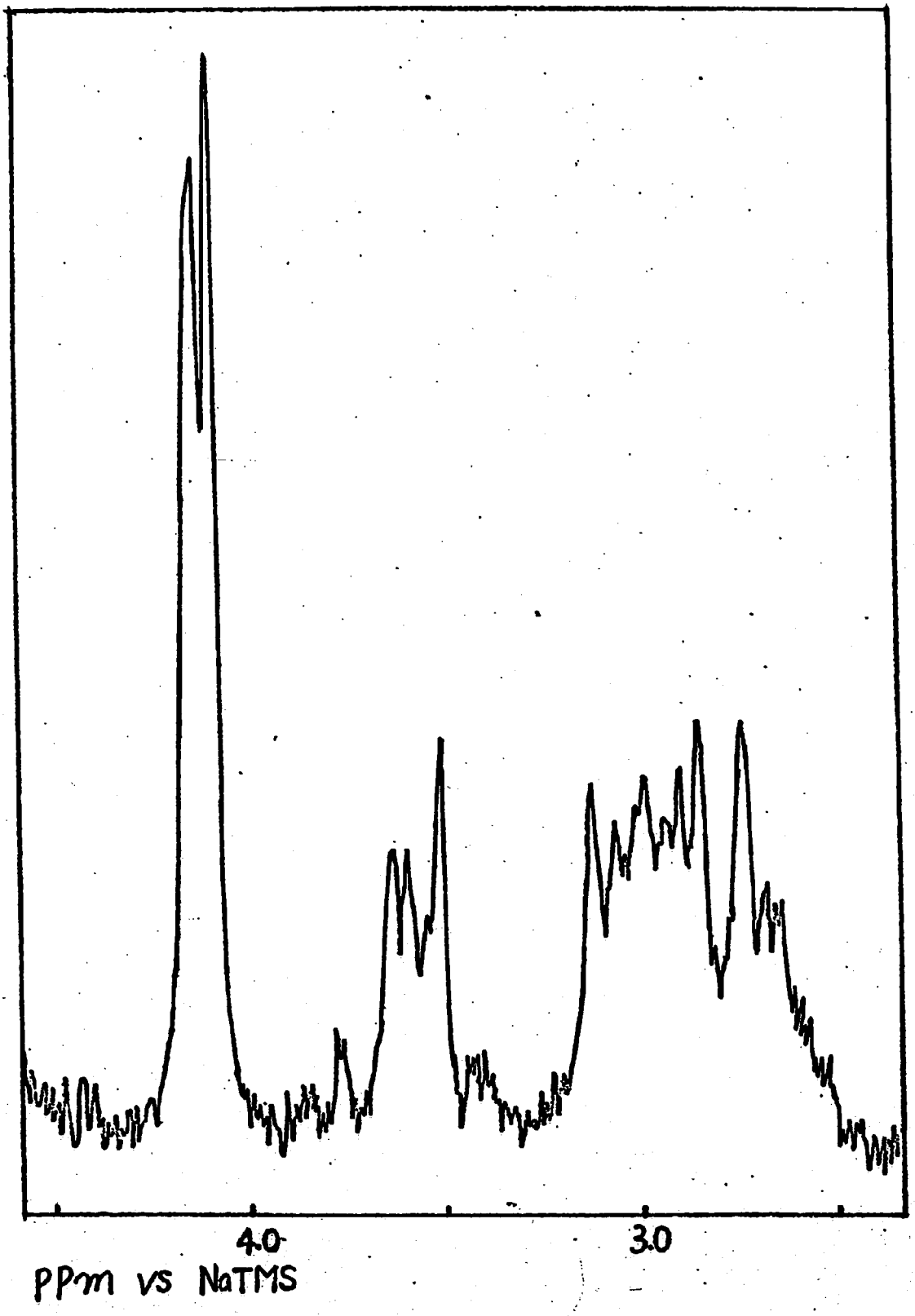


Figure X

Nmr spectrum of <u>cis</u>-[Co(en)(β-AEID)]$^{+}$.

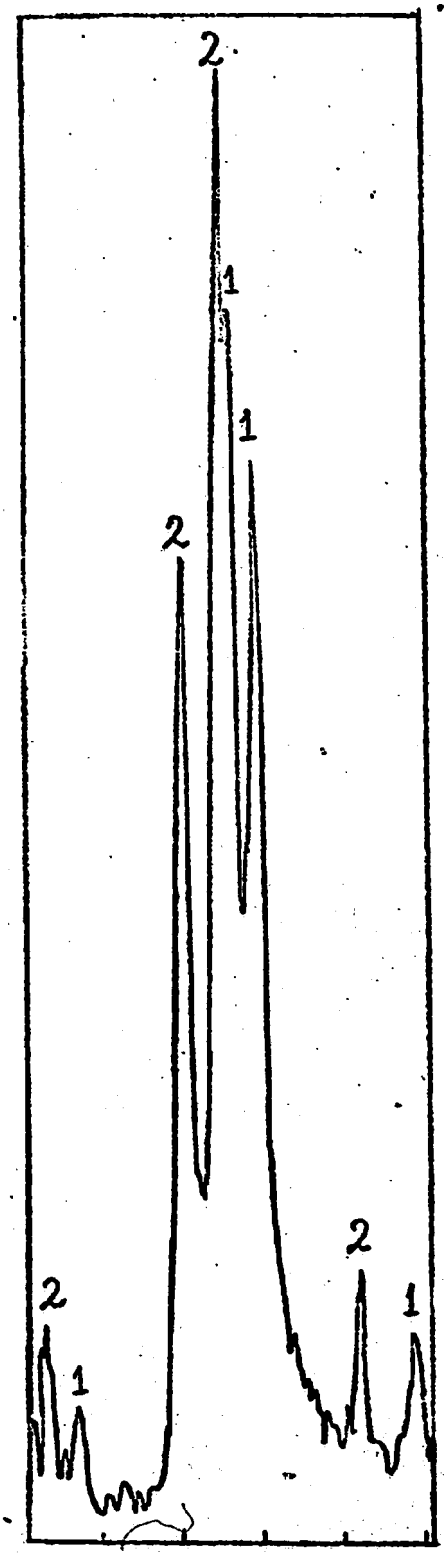


Figure XI

Nmr spectrum of cis-[Co(en)(β-AEID)]$^{+}$ in the acetate ring protons region at 100 Mc/sec.

E. Optical Rotatory Dispersion and Circular Dichroism Spectra

For the cis-[Co(l-pn)(β-AEID)]$^{+}$ ion, because of the fact that the Co^{+3} is at the center of dissymmetry and is making use of an optically active ligand l-pn, two diastereoisomers are possible. Because l-pn is asymmetric two positional isomers are also possible. So a total of four isomers Dl_1, Dl_2, Ll_1 and Ll_2 are possible for this cis isomer, where D and L are used to represent the two optical configurations of the cis isomer and l_1 and l_2 used to represent the two ways of orientation of the l-pn. For cis-[Co(l-chxn)(β-AEID)]$^{+}$, because of the same reasons two diastereoisomers are possible. However there will be no positional isomers because the l-chxn is symmetrically coordinated.

For trans-[Co(l-pn)(β-AEID)]$^{+}$, the tetradeutate exhibits a plane of symmetry and no configurational isomers exist, only positional isomers due to the two orientations of l-pn exist. For trans-[Co(l-chxn)(β-AEID)]$^{+}$, because of the plane of symmetry of the tetradentate and the fact that l-chxn will be symmetrically coordinated, only one isomer should form.

All the ORD and CD curves for trans- and cis-[Co(l-pn)(β-AEID)]$^{+}$ and [Co(l-chxn)(β-AEID)]$^{+}$ are shown from Figure XII to Figure XIX. The CD extrema associated with the first and the second absorption bands are tabulated in Table I.

I. ORD and CD Curves for Trans-[Co(l-diamine)-(β-AEID)]$^{+}$ Ions

The Cotton effects as shown in their ORD and CD curves in Figure XII and XIV are due to the vincinal effect alone as there is no configurational contribution in these complexes.

The order of magnitude of ORD and CD curves are reasonable for vincinal effect. The maximum molar rotations is about 800-1000°

occurring at about 2.1 x $10^4 cm^{-1}$ (see Figure XII) and maximum CD is about 0.13→0.18 occurring at 2.2 x $10^4 cm^{-1}$ (see Table I and Figure XIV).

As discussed in the introduction, in various kinds of complexes which contain optically active diamines of same configuration, it has been found that the induced Cotton effects by these amines are of the same sign in corresponding electronic transitions for a given complex (30). Since the diamines l-pn and l-chxn have the same absolute configurations (30,58,59) it is expected that the ORD and CD curves of the trans-complexes will have similar shapes. As shown in Figure XII, the ORD curves of these trans isomers have similar shapes and the CD curves shown in Figure XIV again reveal general similarities. There are two CD bands in $^1A_{1g} \rightarrow {}^1T_{1g}$ transition. The major CD for all the trans-compounds occur at 2.2 x 10^4 cm, corresponding to the shoulder on the higher energy side of the first absorption band (Table I), and are positive in sign. The CD spectra in the region from 1.5 x 10^4 cm^{-1} to 2.0 x 10^4 cm^{-1} appear to be a composite of two peaks; a positive peak at 1.85 x 10^4 cm^{-1} and a negative peak at 2.0 x 10^4 cm^{-1}. The relative intensity of these two peaks affect the overall appearance of the CD spectra in this region. In the trans-[Co(l-chxn)(β-AEID)]$^+$ the relative intensity of the positive peak is greater and the CD spectrum is generally positive with a negative portion at 1.6 x 10^4 cm^{-1} due to the broad negative peak. In the spectra of the l-pn complexes the intensity of the negative peak is somewhat greater than the positive giving the resulting peak and node seen in the CD spectra. It would be expected that l-pn and chxn would have slightly different influences on the environment of the Co^{+3}. This could result in the different relative intensities of these two CD peaks.

2. ORD and CD Curves for the Cis-[Co(l-diamine)(β-AEID)]$^+$ Ions

(a) Cis-[Co(l-chxn)(β-AEID)]$^+$ Ion

For the unresolved cis-[Co(l-chxn)(β-AEID)]$^+$, the ORD curve Figure XIII and CD curve Figure XV have essentially the same character as that of the trans series. There are two positive CD bands in the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition. The major CD band occurring at 2.2×10^4 cm^{-1} has an intensity of +0.31 and the minor CD band occurring at 1.9×10^4 cm^{-1} has an intensity of +0.15. The molar rotation has a maximum of about 1000° at 2.04×10^4 cm^{-1} (see Figure XIII). The slight increase in intensity in the CD curves of cis in comparison to the corresponding trans compound could be due either to a greater than 50:50 ratio of $(+)_{500}$-cis to $(-)_{500}$-cis formation or to a change in interligand interactions from trans to cis.

(b) Cis-[Co(l-pn)(β-AEID)]$^+$ Ions

As mentioned before for this cis complex ion, it is possible to have two configurational and two positional isomers. The combination makes it possible to have four diastereoisomers.

From the ORD curves Figure XVI and CD curves Figure XVII of $(+)_{500}$-cis-2-[Co(l-pn)(β-AEID)]$^+$, it is observed that the maximum molar rotation as well as CD extrema are about five times greater in this isomer than in the unresolved cis-[Co(l-chxn)(β-AEID)]$^+$ or the trans-[Co(l-pn or l-chxn)(β-AEID)]$^+$ complexes. Although the CD extrema occur in Table I at 2.2×10^4 and 1.8×10^4 cm^{-1} as in the unresolved cis-[Co(l-chxn)(β-AEID)]$^+$or [Co(l-pn or l-chxn)(β-AEID)]$^+$(see Table I), the major band has reversed, being at lower energy side at 1.9×10^4 cm^{-1} and having an intensity of -1.21. The maximum molar rotation which occurs

at 2.0×10^4 has a value of 5500° which is large for vincinal effect alone. Furthermore the essentially mirror image relationship between the ORD and CD curves of $(-)_{500}$-cis-[Co(l-pn)(β-AEID)]$^+$ and $(+)_{500}$-cis-2-[Co(l-pn)(β-AEID)]$^+$ suggests that there are configurational effects as well as vincinal effects in these two complexes. In other words, the $(-)_{500}$-cis and $(+)_{500}$-cis-2-[Co(l-pn)(β-AEID)]$^+$ are essentially diastereoisomers in which the tetradentate ligands have enantiomeric relationships. Although it is possible that in these isomers the orientation of l-pn may be different, the Cotton effects generated by different orientation of l-pn should be very similar as seen in the case of the trans isomers with l-pn. The vincinal effect denoted as VE (see Figures XIII, XV and Table I) in the $(+)_{500}$-cis-2- and $(-)_{500}$-cis-[Co(l-pn)(β-AEID)]$^+$, is obtained by adding the ORD and CD curves of $(+)_{500}$-cis-2 and $(-)_{500}$-cis-[Co(l-pn)(β-AEID)]$^+$ and divided by two, under the assumption that the configurational and vincinal effect are additive in these complexes. As shown in Figure XIII and Figure XV, the ORD and CD curves of the vincinal effect so obtained have similar character as that for the unresolved cis-[Co(l-chxn)(β-AEID)]$^+$ where the Cotton effects are thought to be contributed mainly by vincinal effect. The intensity of this calculated vincinal effect is again of the right order. The major peak occur at the higher energy side of the first absorption band at 2.2×10^4 cm^{-1} as for all the trans series compounds of this type and the unresolved cis-[Co(l-chxn)(β-AEID)]$^+$ where vincinal effect alone or mainly contribute to the optical activity.

Since during the column separation of $(-)_{500}$-cis-[Co(l-pn)(β-AEID)]$^+$ only one component was observed in all the fractions in the second cis band and the rotations was essentially constant for all the fractions,

this isomer is probably optically pure. The $(+)_{500}$-cis-2-[Co(l-pn)(β-AEID)]$^+$ was isolated from the first cis band that had several components and various maximum rotations, so this fraction probably contains several possible isomers. This fraction hence may not be optically pure. But if we suppose the vincinal effect in this cis-[Co(l-pn)(β-AEID)]$^+$ is approximately equal to that in trans-[Co(l-pn)(β-AEID)]$^+$or the unresolved cis-[Co(l-chxn)(β-AEID)]$^+$, the fact that the calculated vincinal effect is quite close to the observed vincinal effect indicates that $(+)_{500}$-cis-2-[Co(l-pn)(β-AEID)]$^+$ is essentially pure. If we accept this we then may proceed to get two ORD and CD curves by subtracting the vincinal effect in cis-[Co(l-chxn)(β-AEID)]$^+$ (denoted as VE') from the complexes $(+)_{500}$-cis-2- and $(-)_{500}$-cis-[Co(l-pn)(β-AEID)]$^+$ to get pure configurational effect due to asymmetric distribution of the tetradentate ligand. These curves are shown in Figure XVIII and XIX. These curves can not be taken as quantitative since the optical purity of one of the diastereoisomer is not known. However, if we accept the assumption just made, these curves will qualitatively represent the configurational effect in $(+)_{500}$-cis-2 and $(-)_{500}$-cis complexes. Here the major band occurs at lower energy side of the first band at 1.9×10^4 cm^{-1} and the minor band occurs at 2.2×10^4cm^{-1} reversing the order for the calculated VE in this system or the vincinal effect VE' in [Co(l-chxn)(β-AEID)]$^+$. If the configurational effect contribute most to ^1E_a and vincinal effect contribute most to $^1A_2$ as for the compounds studied by Douglas et al. (32,33), we would assume that ^{1}Ea lies at the lower energy side of the first band. However if we take CF theory prediction (52,53,54), the lower energy side CD band will be the $^1A_2$ transition.

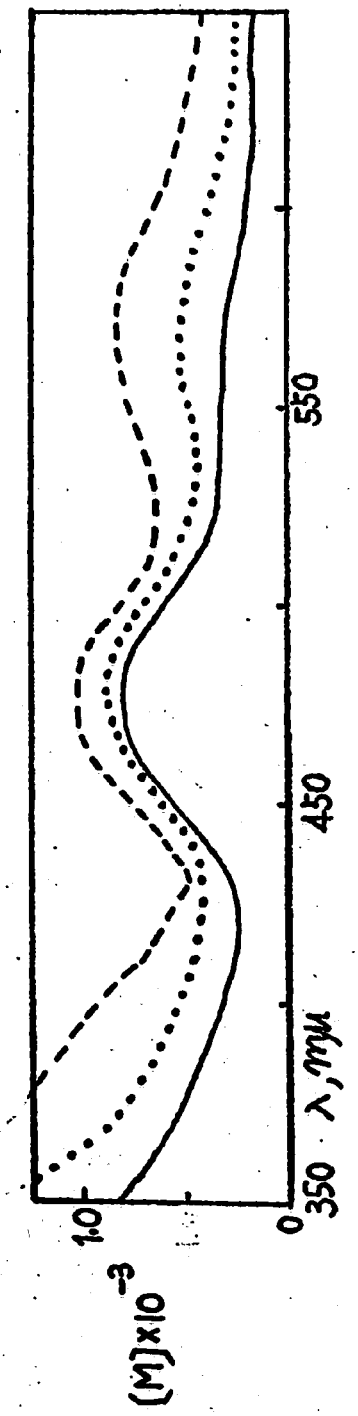


Figure XII. ORD Curves of trans-T_1-[Co(l-pn)(β-AEID)]$^+$, trans-T_2-[Co(l-pn)(β-AEID)]$^+$ ..., and trans-[Co(l-chxn)(β-AEID)]$^+$ ---.

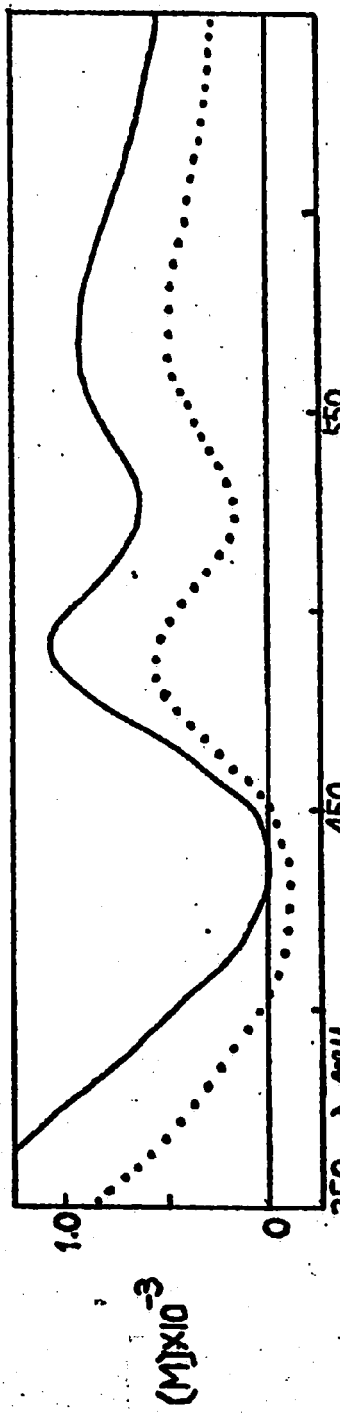


Figure XIII. ORD curves of cis-[Co(l-chxn)(β-AEID)]$^+$ —, and VE in cis-[Co(l-pn)(β-AEID)]$^+$ .....

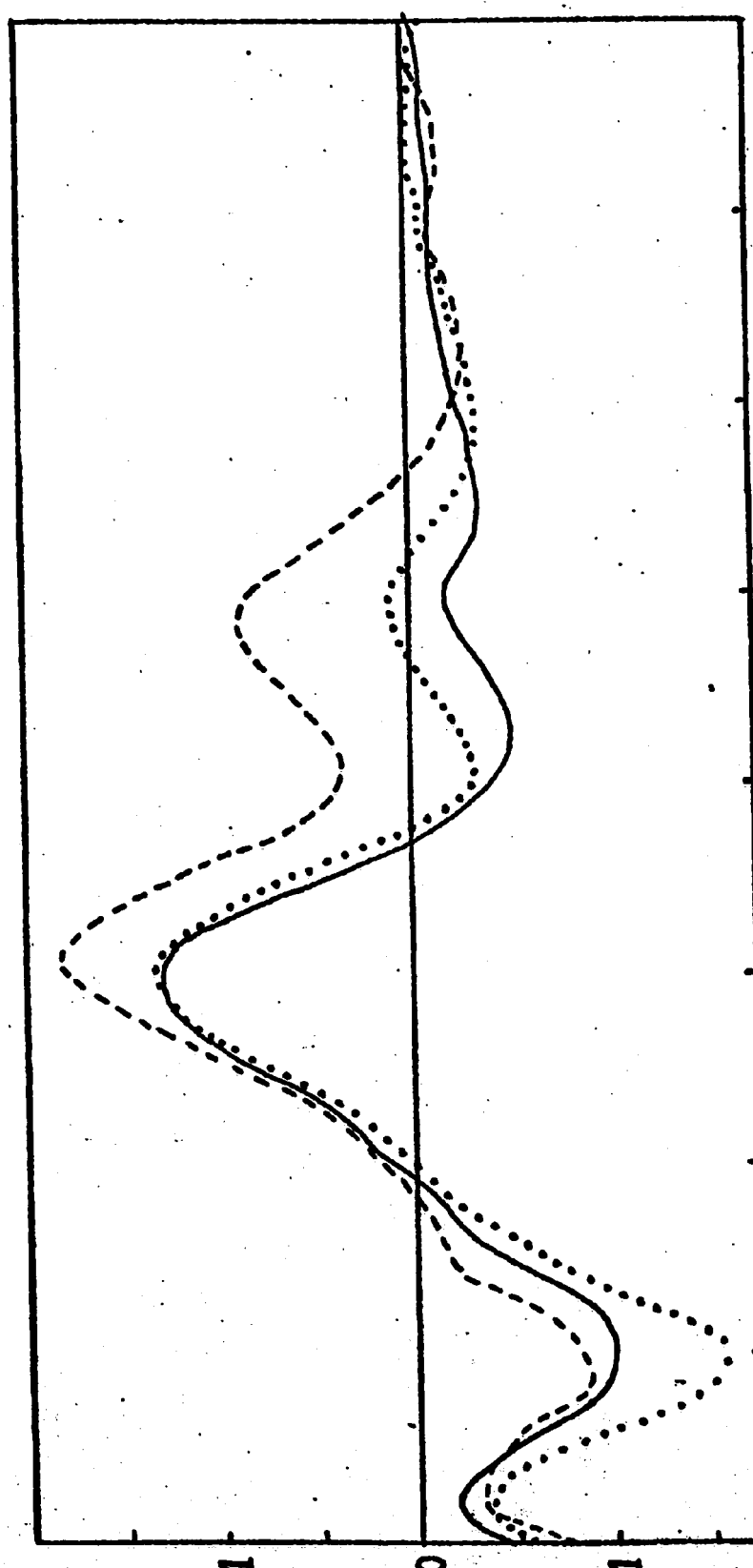


Figure XIV. CD spectra of trans-T_1-[Co(l-pn)(β-AEID)]$^+$ —, trans-T_2-[Co(l-pn)(β-AEID)]$^+$ ····, and trans-[Co(l-chxn)(β-AEID)]$^+$ – – –.

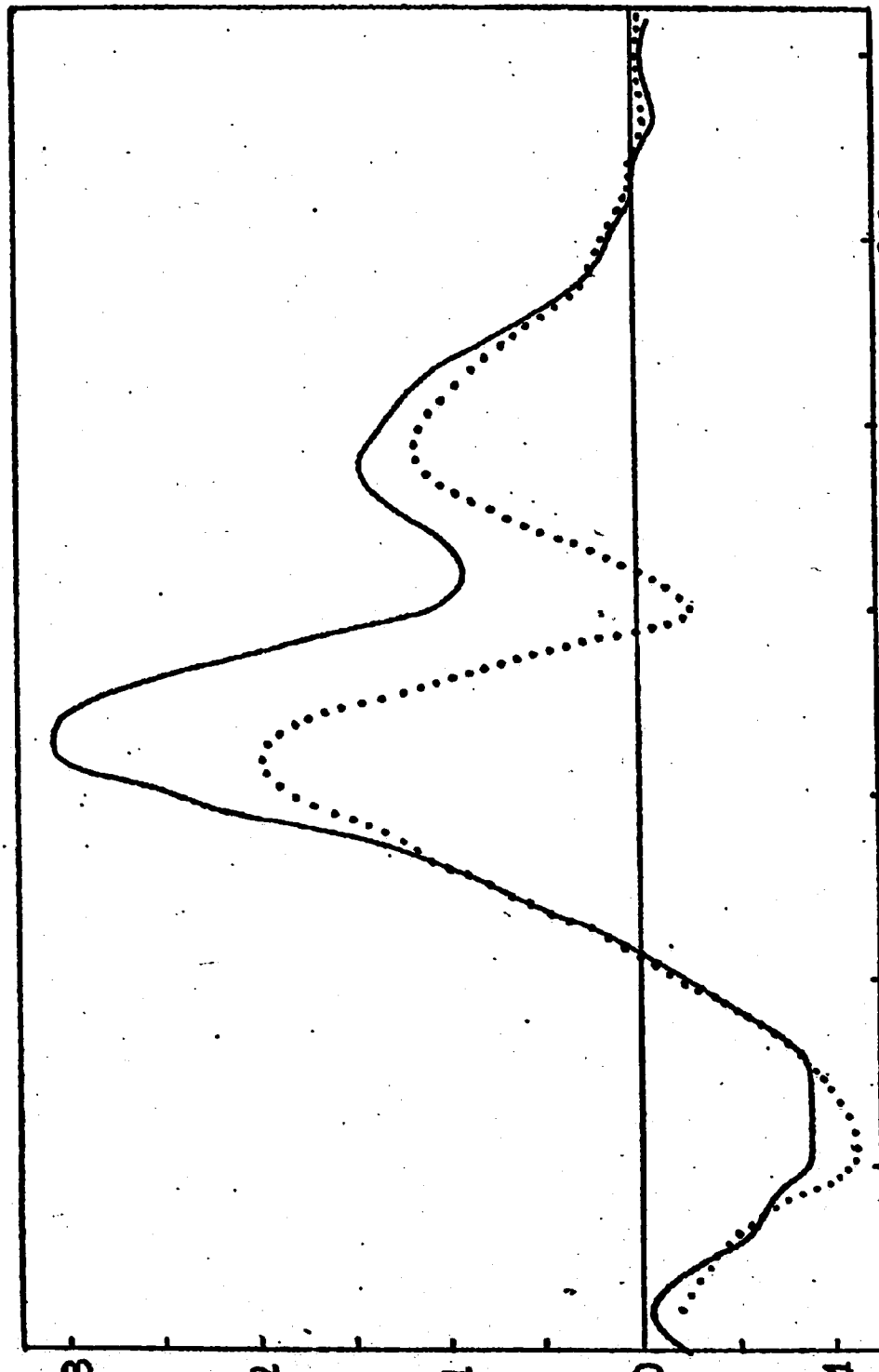


Figure XV. CD spectra of cis-[Co(l-chxn)(β-AEID)]$^+$——, and VE in cis-[Co(l-pn)(β-AEID)]$^+$....

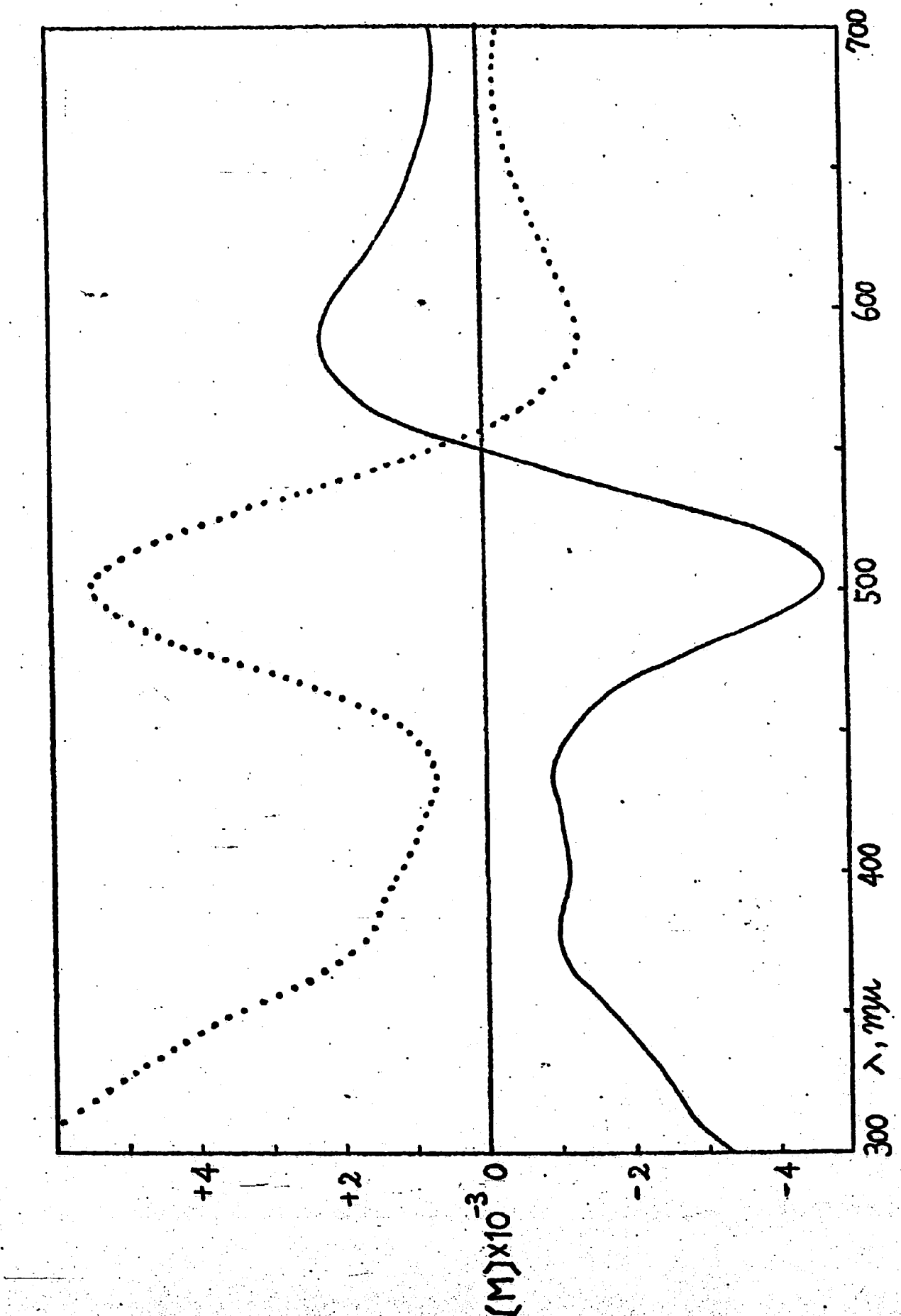


Figure XVI. ORD curves of (-)$_{500}$-*cis*-[Co(*l*-pn)(β-AEID)]$^{+}$ ——, and (+)$_{500}$-*cis*-2-[Co(*l*-pn)(β-AEID)]$^{+}$ ....

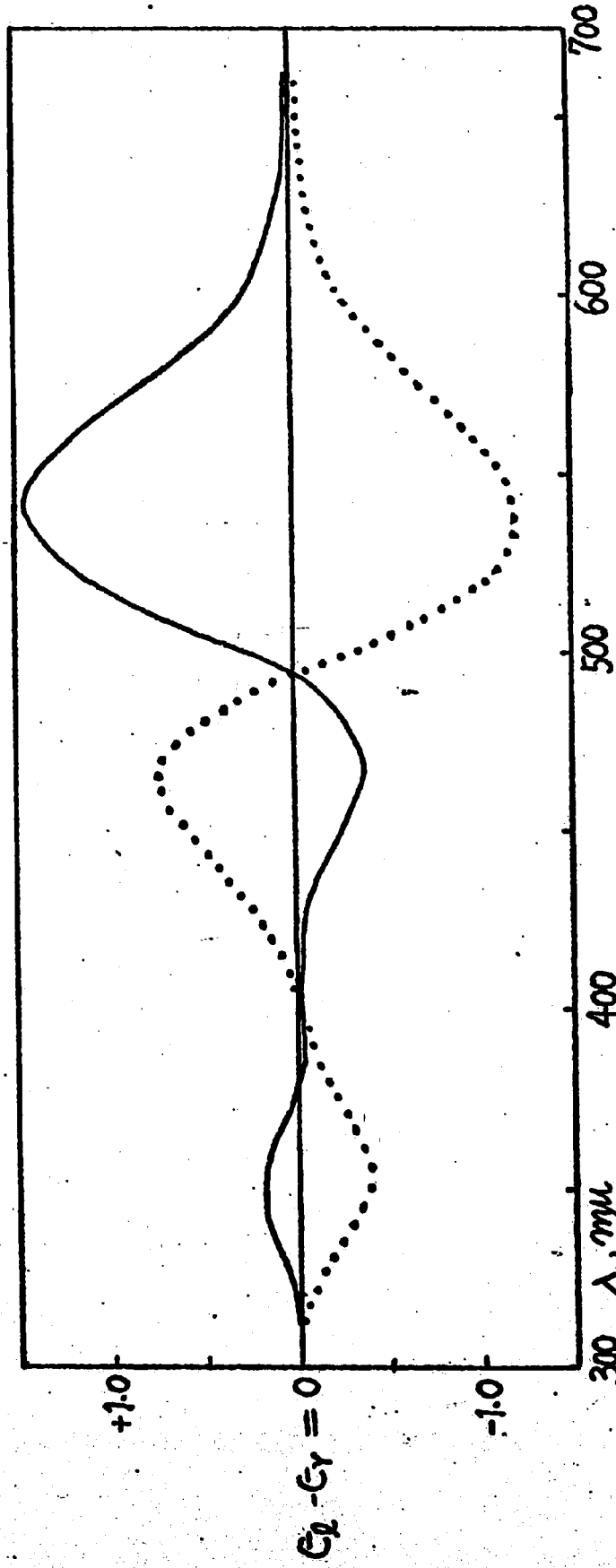


Figure XVII. CD spectra of $(-)_{500}$-cis-[Co(l-pn)(β-AEID)]$^+$—, and $(+)_{500}$-cis-2-[Co(l-pn)(β-AEID)]$^+$....

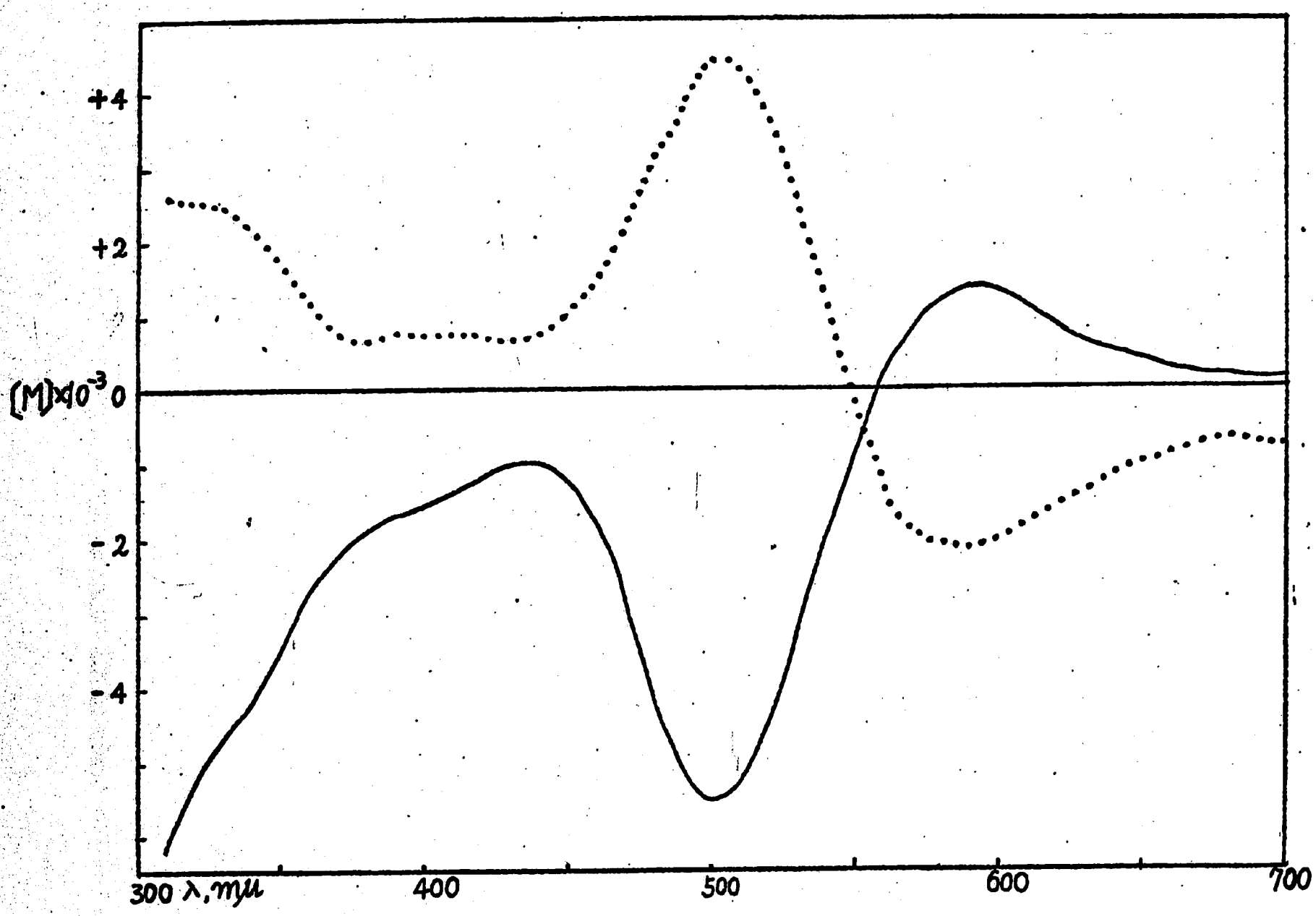


Figure XVIII. ORD curves of (-)$_{500}$-cis-[Co(l-pn)(β-AEID)]$^{+}$ minus VE' —, and (+)$_{500}$-cis-2-[Co(l-pn)(β-AEID)]$^{+}$ minus VE' ....

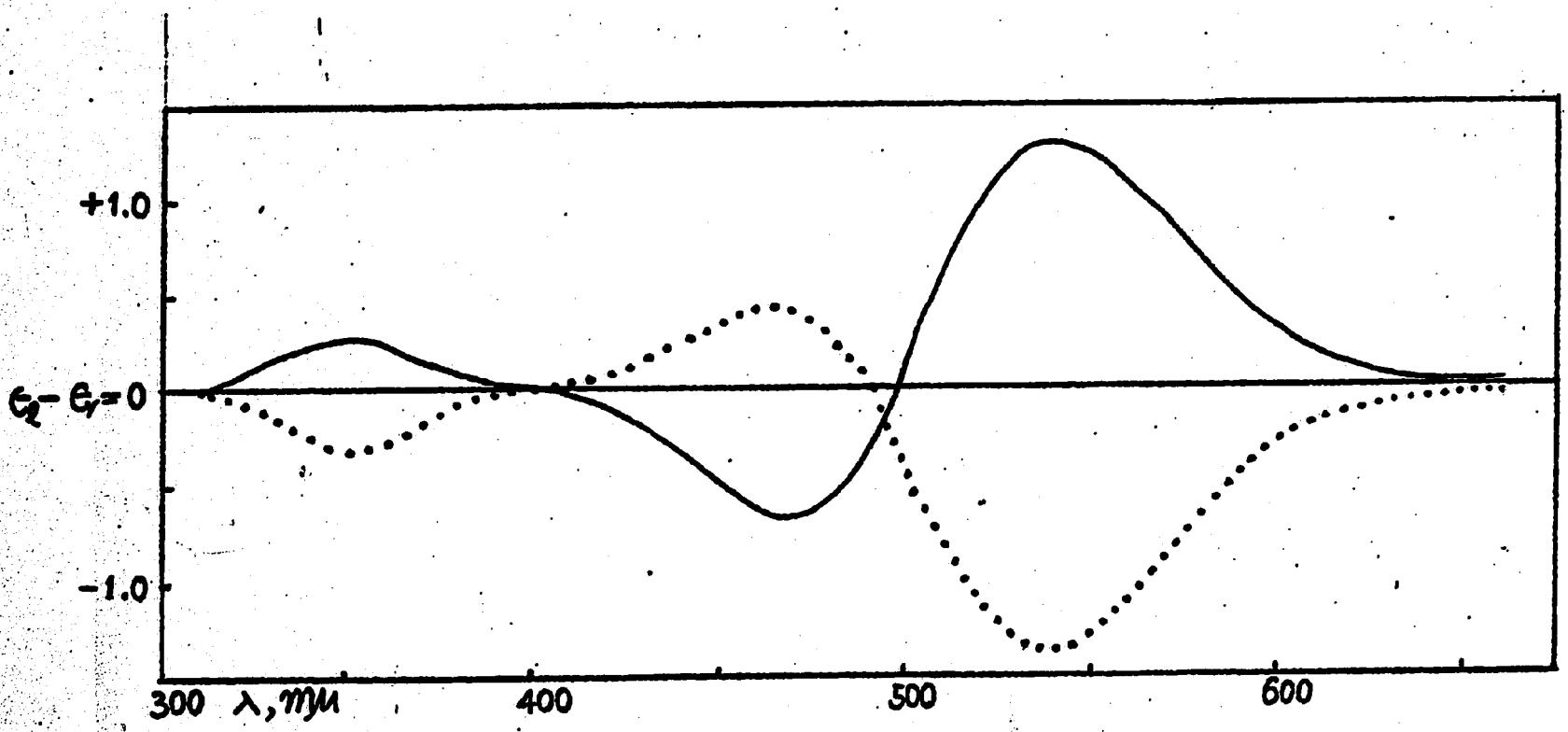


Figure XIX. CD spectra of $(-)_{500}$-cis-[Co(l-pn)(β-AEID)]$^+$ minus VE' ——, and $(+)_{500}$-cis-2+[Co(l-pn)(β-AEID)]$^+$ minus VE'....

The mere presence of optical activity due to configurational effect in cis-[Co(l-pn)(β-AEID)]$^+$ complex shows that there are factors other than conformation of ring or helical arrangement of bidentate rings around metal ion which contribute to optical activity. The major factor which determines the configurational effect in these cis complexes is the difference between an coordinated oxygen and nitrogen. Since according to the definition of octant sign (36) which neglects the contributions of coordinated atoms to optical activity and includes only the position of ring atoms, the configurational effect of cis compounds will have no octant sign and hence no optical activity. Again according to ring pairing method (21) which consider a N-N ring as the same as a N-O ring, the present complex will have no configurational effect and be optically inactive.

Because of the fact that the current rules have been designed to correlate configurations of complexes whose optical activity is due to the spiral arrangement of bidentate rings around metal ion or due to conformation of optically active ligand without considering the difference between the coordinated atoms, the configuration of $(+)_{500}$-cis-2- or $(-)_{500}$-cis-[Co(l-pn)(β-AEID)]$^+$ can not be assigned by comparing Cotton effect in a related transition with them.

In order to relate configuration of these cis complexes, the configuration have to be redefined by including a sign for each coordinated atom such as nitrogen and oxygen in terms of octant rule (35). In terms of ring pairing method (21), it is important to decide which of the two sets of helical ring systems (N-N, N-O) or (N-N, N-N) determines the net chirality. Also the transition that is related to configuration in the resolved cis complex should be identified.

V. SUMMARY

Two tetradentate ligands bis-(β-aminoethyl)iminoacetic acid trihydrobromide and β-aminoethyliminodiacetic acid hydrosulfate were prepared. Their various cobalt (III) complexes were made by reacting with carbonatotetraamminecobalt (III) ion followed by acidification and addition of a bidentate or two monodentate ligands.

The $[Co(en)(Bis\text{-}\beta\text{-AEIA})]^{+2}$ ion was identified as being cis in configuration by its nmr spectrum. The geometrical isomers of all the $[Co(diamine)(\beta\text{-AEID})]^{+}$ type of complexes where the diamine is en, l-chxn or l-pn were separated on cation exchange column. The trans and cis isomers of $[Co(en)(\beta\text{-AEID})]^{+}$ were identified by visible and nmr spectra. The trans and cis isomers of $[Co(l\text{-chxn})(\beta\text{-AEID})]^{+}$ and $[Co(l\text{-pn})(\beta\text{-AEID})]^{+}$ were identified by their visible spectra.

The ORD and CD curves of the trans-$[Co(l\text{-chxn})(\beta\text{-AEID})]^{+}$ and $[Co(lpn)(\beta\text{-AEID})]^{+}$ were the result of vincinal effects alone. The ORD and CD curves of cis-$[Co(l\text{-chxn})(\beta\text{-AEID})]^{+}$ may or may not have some configurational effect depending on the ratio of diastereoisomers formed in this isomer. The ORD and CD curves of the cis-$[Co(l\text{-pn})(\beta\text{-AEID})]^{+}$ can be attributed to both configurational and vincinal effects.

The resolution of cis-$[Co(l\text{-pn})(\beta\text{-AEID})]^{+}$ indicates that there are factors other than the spiral arrangement of chelate rings around metal ion or conformation of rings which contribute to optical activity and in define chirality the coordinated atoms should be taken into consideration.

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