CIRCULAR DICHROISM STUDIES OF SOME DISSYMMETRIC COORDINATION COMPOUNDS

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DEDICATED

TO

MY WIFE AND CHILDREN

CERTIFICATE

This is to certify that this dissertation submitted by **MR. SYED RAUF** is accepted in its present form by the Department of Chemistry, Quaid-i-Azam University Islamabad (Pakistan) as satisfying the dissertation requirements for the degree of Doctor of Philosophy in Chemistry.

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ABSTRACT

CIRCULAR DICHROISM STUDIES OF SOME DISSYMMETRIC COORDINATION COMPOUNDS

The Pfeiffer effect is a change in optical rotation of a chiral organic compound or complex ion (the environment substance) in solution upon the addition of certain racemic metal complexes.The Pfeiffer effect was investigated in a series of racemic complexes in presence of various chiral environment substances. A number of mixed ligand complexes such as cis-$[Cr(phen)_2Cl_2]^+$, $[Cr(phen)_2ox]^+$, cis-$[Cr(bpy)_2Cl_2]^+$, $[Cr(bpy)_2gly]^{2+}$ cis-$[Cr(bpy)_2(H_2O)]^{3+}$ and $[M(EDTA)]^-$, $[M(DTPA)]^-$ ($M = Cr^{3+}$, V^{3+}), $[Co(BPA)_3]^{2+}$, $[Cu(2\text{-}ampy)_2]^{2+}$ and $[Nd(EDTA)]^-$ show the Pfeiffer effect in presence of (+)-cinchonine HCl (-)-cinchonidine HCl, (+)-tartaric acid, (+)-ascorbic acid, (+)-α-methylbenzylamine HCl, (-)-ephedrine HCl and/or (-)-brucine HCl. Most of these complexes show a positive Pfeiffer effect in presence of various environment substances. However (+)-cinchonine HCl and (-)-cinchonidine HCl induced a negative Pfeiffer effect in mixed ligand complexes of chromium(III), Na[V(EDTA)] and $Na_2[V(DTPA)]$. A few new environment substances like (+)-α-methylbenzylamine HCl, (-)-ephedrine HCl, (-)-cinchonidine HCl and (+)-ascorbic acid have been found to induce the Pfeiffer effect in some of these complexes.

CD spectra of the Pfeiffer systems in aqueous solutions were measured. The mixed ligands chromium(III) complexes show 1-2 Cotton bands in visible region. The band I is observed between 16,666-16949 cm^{-1} and a higher energy band II between 19,607-20,000 cm^{-1}. These bands are assigned to electronic transition to A_1 and B_1 upper states respectively. The CD spectra of $[Cr(EDTA)H_2O]^-$ ion in presence of (+)-tartaric acid and (+)-ascorbic acis has a broad band at 17,857 cm^{-1} while that in presence of (+)-cinchonine HCl and (-)-cinchonidine HCl consist of an additional weak Cotton band of opposite sign at 20,408 cm^{-1}. $[Cr(DTPA)]^{2-}$ shows a stronger positive Cotton band at 19,230 cm^{-1} and a weaker negative CD band at 23,809 cm^{-1} in presence of (+)-tartaric acid and (+)-α-methylbenzylamine HCl. In presence of (+)-ascorbic acid a mirror image spectrum is obtained. These two Cotton bands are assigned to electronic transitions $^4A_2 \longrightarrow {}^4A_1$ and $^4A_2 \longrightarrow {}^4B_2$ respectively.

CD spectra of $[V(EDTA)]^-$ in presence of (-)-cinchonidine HCl, (+)-α-methylbenzylamine HCl, (-)-brucine HCl and (+)-tartaric acid has a positive Cotton band at 19,607 cm^{-1} and a negative weaker band at 23,255 cm^{-1}. $[V(DTPA)]^2$ shows Cotton bands at 15,873 cm^{-1} and at 21,276 cm^{-1} which are assigned to $^3A_1 \longrightarrow {}^3A_2$ $({}^3T_1g(P)$ and $^3A_1 \longrightarrow {}^3B_1$ $(T^3{}_1g(P))$ transition respectively. CD spectra of $[Co(BPA)_3]^{2+}$ in presence of ammonium-(+)-α-bromocamphorsulphonate and (-)-10-camphorsulphonic acid has a couplet of oppositely signed Cotton bands centered at 18,348 cm^{-1} and 21,505 cm^{-1}. These are assigned to $^4A_2 \longrightarrow {}^4A_1$ and $^4A_2 \longrightarrow {}^4E_1$ transition respectively.

$[Nd(EDTA)]^-$ shows a negative CD band at 17,871 cm^{-1} in presence of (+)-tartaric acid and (-)-cinchonidine HCl which is due to f $\longrightarrow$ f transition. The binuclear complexes of Vanadium (III) like $[V_2(AA)_4(\mu\text{-}OH)_2]^{+4}$ (AA = phen or bpy) exhibited strong charge transfer CD bands in presence of (+)-tartaric acid. These two binuclear species were precipitated out as perchlorate salts. The elemental analysis and IR spectra of the solid perchlorate complexes indicated that tartarate ion has been coordinated to Vanadium (III) replacing hydroxo bridges. The complex ions $[V_2(phen)_4(\mu\text{-}(+)\text{-}tart)]^{+4}$ and $[V_2(bpy)_4(\mu\text{-}OH)(\mu\text{-}(+)\text{-}tart)]^{3+}$ slowly oxidized to a green mononuclear species which could also be precipitated as perchlorate salts. Elemental analysis of this green compound fits well in cis-$[VO(bpy)_2Cl](ClO_4)$. It is indicated from these studies that anasymmetric synthesis of (+)-$[VO(bpy)_2Cl](ClO_4)$ has been achieved during oxidation of its binuclear analog.

The absolute configuration of ligands around the metal ions in these complexes have been assigned on the basis of the sign of Pfeiffer effect in presence of various environment substances and CD spectra of the Pfeiffer systems. The *leva* enantiomers of the complexes cis-$[Cr(phen)_2Cl_2]^+$, cis-$[Cr(bpy)_2Cl_2]^+$, $[Cr(bpy)_2gly]^{2+}$ cis-$[Cr(bpy)_2(H_2O)_2]^{3+}$ and *dextra* enantiomer of $[Cr(phen)_2ox]^+$ are assigned "Δ" absolute configuration. Similarly (+)-Na[Cr(EDTA)H_2O], (+)-Na_2[Cr(DTPA)] and (-)-Na[V(EDTA)], (-)Na_2[V(DTPA)] and (+)-$[Co(BPA)_3]^{2+}$ have also been assigned "Δ" absolute configuration. The binuclear complexes (+)-[V_2(phen)$_4$(μ-(+)-tart)](ClO_4)$_4$ and (+)-[V_2(bpy)$_4$(μ-OH)(μ-(+)-tart)](ClO_4)$_3$ are assigned "Δ" absolute configuration while the mononuclear (+)-cis-[VO(bpy)$_2$Cl]ClO_4 is assigned "Λ" absolute configuration.

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CHAPTER 1

INTRODUCTION

The Pfeiffer effect is a change in the optical rotation of a chiral organic compound in presence of certain racemic metal complexes. This effect was first noticed by P.Pfeiffer in 1931[1-3], who reported a decrease in optical rotation of d-10-camphorsulphonic acid in presence of $[Zn(phen)_3]^{2+}$. It was also observed that optical rotation of d-(+)-bromocamphor-π-sulphonate ion is increased in presence of $[Zn(phen)_3]^{2+}$ ion. Later this anomalous change in optical rotation was named after its discoverer as the Pfeiffer effect. The shift in optical rotation can go in either direction. If the optical activity of the chiral compound (called the environment substance) is increased in presence of the racemic complex, it is termed as a positive Pfeiffer effect and if decreased then it is known as negative Pfeiffer effect. Later studies showed that a number of tris complexes of '3d' metal ions such as Mn^{2+}, Co^{2+}, Ni^{2+} and Cu2+ with 1,10-phen and 2,2-bipy show this effect in presence of chiral compounds like (-)-10-camphor sulphonic acid, (+)-α-bromocamphor-π-sulphonate, (+) and (-)-tartaric acid, (+) and (-)-malic acid and and (+)-cinchonine HCl. It was also observed[4] that the magnitude of this effect is dependent upon the conecntration of the complex and environment substance wavelength of light and temperature of the system. It is generally accepted that origin of the Pfeiffer effect lies in the dissymmetric metal complex. At present there exist two theories about the origin and mechanism of this effect.

1. Equillibrium Displacement theory (also called as configurational activity): This theory is based upon the concept that an asymmetric electric field caused by the stable optically active species, contributes to the activity coefficients of the 'd' and 'l'metal complex antipodes. This leads to a displacement in the racemic equillibrium (i.e; 50:50), producing a change in the optical rotation of the system.

2. Hydrophobic bonding theory:

According to this theory when a species stable with respect to racemization (i.e; environment compound) is added to a solution containing an optically labile species (i.e; racemic complex), an association takes place between the two. This association between the racemic complex and the environment is termed as "hydrophobic bonding. "This can be represented by an equillibrium equation as

$$d,l\ [Zn(phen)_3]^{2+} + \underset{(1-X)}{d\text{-}\alpha\text{-}BCS} = \underset{(X)}{d[Zn(phen)_3](d\text{-}\alpha\text{-}BCS)^+} + l[Zn(phen)_3](d\text{-}\alpha\text{-}BCS)$$

Where 'X' is the fraction distribution. Whenever x is greater or less than 0.5, a change in rotation will be observed. Dwyer and coworkers[5] have reported a number of experiments strongly supporting the concept of equillibrium shift which results in configurational activity. From these investigations it was found that environmental variables such as ligand, active species, solvent and oxidation state of the metal ion have a profound effect upon the optical rotation of the system. Later studies by Kirschner et.al[6] also supported the equillibrium displacement theory.

The hydrophobic bonding theory was proposed and supported by a number of experiments by Brasted and coworkers[7]. These workers plotted optical rotation (α) or refractive index (n) of a series of systems containing different mole fractions of $[Zn(phen)_3]^{2+}$ and ammonium-(+)-α-bromocamphorsulphonate or (-)-strychnine sulphate and concluded that some association between the racemic complex and active environment existed. On the basis of conductivity measurements of varying concentrations of $[Zn(phen)_3](BCS)_2$and $[Zn(en)_3](BCS)_2$,they termed these complexes as weak electrolytes, suggesting a partial dissociation of the complex in aqueous solution. It was found by a cryoscopic method that nearly 50 % of the complex $[Zn(phen)_3](BCS)_2.H_2O$ was dissociated in aqueous solution. Both of these theories agree that the origin of Pfeiffer effect lies in dissymetric complexes. The difference in these theories is that equilibrium displacement theory suggests a slight shift in racemic d = 1 equillibrium towards left or right under the influence of the environment substance, whereas the second theory presumes an association between the racemic complex and the chiral environment substance. In Pfeiffer systems one enantiomer of the complex favours the bond formation (association) with chiral compound, which ultimately leads to a shift in equillibrium towards the favourable enantiomer of the complex i.e. either 'd' or 'l' side.

It was observed by Kirschner et.al.[8] that optical rotatory dispersion and circular dichroism spectra of the Pfeiffer systems of $K_3[M(C_2O_4)_3]$ where ($M = Co(III), Cr(III)$) were similar to those of their resolved enantiomers. From the optical rotatory dispersion and circular dichroism spectral studies these workers concluded that dissymmetric complexes were responsible for the Pfeiffer effect. These workers[9] have used the Pfeiffer effect for partial resolution of complex ion such as $[Ni(phen)_3]^{2+}$, $[Ni(bipy)_3]^{2+}$, $[Cr(ox)_3]^{3-}$ and $[Co(ox)_3]^{3-}$ as well. They allowed the Pfeiffer effect to develope in the initially racemic tris phenanthroline and 2,2-dipyridyl nickel(II) ions in presence of (-)-malic acid and then succeeded in freezing out the non equimolar mixture of enantiomers from the system by precipitation of the enantiometers as insoluble perchlorate salts. These insoluble perchlorate salts were redissolved as chloride by Amberlite-IRA-400 anion exchange resin, and optical rotation of the solutions containing partially resolved complexes ion were measured. In addition they also found that the rate of racemization of the complex resolved by the Pfeiffer effect was similar to that resolved by conventional resolution techniques. In addition to partial resloution, Pfeiffer effect studies are also helpful in determining the absolute configuration of the metal complexes and/or the chiral environment substances Kirschner et.al.[10] proposed a good method for the prediction of absolute configuration of dissymetric metal complexes and dissymetric carboxylic acids based upon their Pfeiffer activity. For this purpose several carboxylic acids were utilized to displace the equilibrium in Pfeiffer systems. It was noted that organic environment substances with "S" absolute configuration gave negative effect, while those with "R" absolute configuration gave a positive effect in $[Co(phen)_3]^{2+}$ and $[Ni(phen)_3]^{2+}$ systems.

Most of the previous work has been done on racemic metal complexes of 1,10-phen, 2,2-bipy, oxalate or hexafloro acetylacetone ligands. Although optical rotatory dispersion and circular dichroism studies of the Pfeiffer active systems is a useful technique, it has not been thoroughly explored. In fact the Pfeiffer effect is not adequately explained by the concept of an equilibrium shift or configurational activity. There is strong evidance in favour of the interaction between the racemic metal complex and the chiral environment by a bonding force i.e. hydrophobic bonding. There seems to be an appreciable contribution from ion pair formation and differential association to the Pfeiffer activity.The relationship between the metal ion and the Pfeiffer effect is not very clear. It was observed[11] that magnitude of the Pfeiffer effect in $[Zn(phen)_3]^{2+}$, $[Cd(phen)_3]^{2+}$ and $[Hg(phen)_3]^{2+}$ ions increase in the order $Hg^{2+} > Cd^{2+} > Zn^{2+}$ which is reverse order of stability. Further only a small group of structurally similar ligands (i.e; 1,10-phen or 2,2- bipy) show this effect. A number of labile dissymmetric complexes of saturated polyamine ligands (en, pn, dien, trien) do not show the Pfeiffer effect, while inert complexes of oxalate ion like $[Co(ox)_3]^{3-}$ and $[Cr(ox)_3]^{3-}$ are Pfeiffer active. The influence of structure of the ligand on Pfeiffer effect is also not clearly understood. Complexes of the same metal ion with different ligands of similar structure behave differently in Pfeiffer effect studies. For example Zn(II)[12] complexes of 1,10-phen and 2,2-bipy show strong Pfeiffer effect in presence of various chiral environment substances while Zn^{2+} complexes of 2,(2-pyridyl)-imidazoline and 2,(2-pyridyl)-benzimidazoline show very weak Pfeiffer activity and those of 2, 2-dipyridyl amine and 2,'2,"2-terpyridyl do not show any Pfeiffer activity at all.

There is no uniform structural relationship between the environment compound and the Pfeiffer activity. Certain chiral enuironment compounds which are structurally very similar, have very different behaviour towards Pfeiffer activity. For instance (+)-cinchonine and (-)-quinine have very similar molecular structures (quinine has an extra $-OCH_3$ group attached to a symmetrical part of cinchonine molecule) but only (+)-

cinchonine induces the effect in many trisoxalate complexes. It is clear from the preceding discussion that further investigations into the Pfeiffer effect in racemic metal complexes are necessary. New Pfeiffer active systems containing dissymetric complexes of new ligands in presence of new chiral environment substances should be explored.

The present work was undertaken to study some new Pfeiffer active systems, and to develope some relationship between structure of the chiral environment, racemic metal complexes and their Pfeiffer activity. In the present studies a number of mixed ligand complexes of the type $[Cr(AA)_2X_2]^{n+}$ where AA= 1,10-phenthroline, 2,2-bipyridine, X = Cl, H_2O, X_2= glycinate or oxalate ion were prepared and studied for the Pfeiffer activity, in presence of optically active environment substances, like (+)-α-methylbenzylamine hydrochloride (α-MBA.HCL), (+)-cinchonine HCl, (-)-cinchonidine HCl,(-)-10-camphorsulphonic acid, ammoium(+)-bromocamphor-π-sulphonate, (-)-malic acid, (+)-tartaric acid, (+)-ascorbic acid, (-)-quinine HCl, (+)-brucine HCl, and (+)-arabinose etc. These complexes exhibited Pfeiffer effect in presence of (-)-cinchonidine HCl, (+)-cinchonine HCl and (+) tartaric acid only. CD spectra of these Pfeiffer systems were recorded and the bands were assigned to various electronic transitions.

The Pfeiffer effect in Cr(III) complexes like $[Cr(malon)_3]^{3-}$, $[Cr(EDTA)H_2O]^{-}$and $[Cr(DTPA)]^{2-}$in presence of all the above mentioned environment compounds was studied. These complexes exhibited Pfeiffer effect with various chiral environment substances, including the new environment compound (+)-α-MBA HCl. CD spectra of these systems were recorded in the visible region. The CD spectrum of tris(malonato) chromate(III) ion was compared and found similar to that of the resolved levo enantiomer.

A number of complexes of the type $[M(BPA)_3](ClO_4)_2$(where BPA = 2,2-bipyridylamine and M = Co^{2+}, Ni^{2+}, Cu^{2+}) were also studied in presence of various chiral environment substances. Only $[Co(BPA)_3]^{2+}$showed Pfeiffer effect in presence of (-)-10-camphorsulphonic acid and NH_4-α-BCS. The CD spectra of these systems is also reported. The complexes $[V(phen)_2Cl_2]Cl$ and $[V(bipy)Cl_2]Cl$ in presence of (+)-T.A showed well defined CD bands in d-d transition region. In aqueous solutions these complexes exist as dimeric ions of the formula $[(AA)_2V(\mu\text{-}OH)_2V(AA)_2]^{4+}$(where AA =2,2-bipy or 1,10-phen). These dimeric complex ions were partially resolved by precipitating as insoluble perchlorate salts. ORD and CD spectra of these partially resolved complexes were recorded. The rates of racemization of these species were also measured. In solution the complex ions $[V_2(AA)_4(\mu\text{-}OH)_2]^{4+}$are rapidly oxidized to green oxavanadium species which have strong CD bands in the visible region. The rate of oxidation in these systems were also measured. Two new complexes $[V(EDTA)]^-$ and $[V(DTPA)]^{2-}$exhibited

Pfeiffer effect in presence of (+)-α-MBA.HCl,(-)-cinchonidine HCl, (-)-ephedrine HCl, (-)-brucine HCl and (+),(-)-tartaric acid. The Pfeiffer CD of these systems were recorded and bands were assigned to various electronic transitions.

CD spectra of $[Pr(EDTA)]^-$ and $[Nd(EDTA)]^-$ in presence of (-)-cinchonidine HCl and (+)-tartaric acid at various pH values were studied.Another complex $[Cu(2\text{-picolyamine})_2](ClO_4)_2$ also exhibited Pfeiffer effect in presence of (-)-10-Camphorsulphonic acid and (+)-α-BCS. CD spectra of these systems are reported.

These studies indicate that equillibrium displacement mechanism is operative in most of the Pfeiffer systems. Presence of pi(π) bonding character in the ligand of metal chelates is necessary for Pfeiffer activity. The Circular Dichroism spectra of Pfeiffer systems may be used for assigning absolute configuration and electronic transitions.

CHAPTER II

NOMENCLATURE AND SYMBOLS

The following abbreviations will be used to simplify the formulas of the coordination compounds and environment substances. The observed Pfeiffer rotation is represented by P_λ where 'λ' represent the wavelength at which the effect is measured. The following equation is used for the calculation of the Pfeiffer effect.

$$P_\lambda = \pm(\alpha_{e+c} - \alpha_e)$$

where α_{e+c} = Observed rotation of the environment plus the complex
α_e = Observed rotation of the environment only

Molar Pfeiffer rotation $[P_M]^t_\lambda$ is calculated using the relation

$$[P_M]^t_\lambda = \frac{P_\lambda}{[c]\times[e]\times d}$$

[c] = Molar concentration of the complex ion,
[e] = Molar concentration of the environment substance,
d = Length of the sample cell in meters.

The ligands, solvents and environment substances are abbreviated as follows:

acac = acetylacetonate ion
ampy = 2-aminomethyl pyridine
(+)-α-BCS = ammonium-α-bromocamphor-π-sulphonate

BBMI = biacetyl-bis-methylimine

bpy = 2,2-bipyridyl

BPA = 2,2-bipyridylamine

(-)-CS = (-)-10-camphorsulphonic acid

Cin.HCl = cinchonine hydrochloride

Cinchd.HCl = cinchonidine hydrochloride

DMF = N,N'-dimethylformamide

DTPA = diethylenetriaminepentaacetate anion

EDTA = ethylenediaminetetraacetate anion

en = ethylenediamine

Ephed.HCl = ephedrine hydrochloride

hfa = hexafluoroacetyl acetonate anion

malon = malonate anion

α-MBA = (+)-α-methylbenzylamine

ox = oxalate anion

phen = 1,10-phenanthroline

pyim = 2-(2-pyridyl)-amidazoline

tart = (+)-tartrate anion

$\Delta\varepsilon$ = $\varepsilon_L - \varepsilon_R$ = difference in molar extinction coefficients of the left and right-handed circularly polarized light, respectively

$[\theta_M]^t_\lambda$ = molar ellipticity in deg.l.mol^{-1}.cm^{-1}

CHAPTER III

HISTORICAL

In 1931 Pfeiffer and Quehl[1-3] discovered the Pfeiffer effect when they were trying to resolve dissymmetirc complexes of zinc(11) ion with bidentate ligands, using d-10-Campphor sulphonic acid. These workers observed that rotation of a solution of zinc camphorsulphonate $Zn(CS)_2.6H_2O$ was decreased upon the addition of three moles of 1,10-phenanthroline. When ammonium-α-bromocamphor- π-sulphonate(BCS) was used instead of camphorsulphonate in this system, an appreciable increase in optical rotation was observed. It had long been recognized that these two resolving agents give opposite enantiomers when used in the resolution of complexes. When the complex was precipitated as bromide salt from a system containing $[Zn(phen)_3](CS)_2$,it was found optically inactive, showing that resolution of the complex did not take place. These authors reported that a solution of zinc sulphate, NH_4BCS and 1,10-pnenanthroline in molar ratio 1:2:3 gave the same optical rotation as a solution containing the same concentration of the complex $[Zn(phen)_3](BCS)_2$. Pfeiffer and co-workers[2,3] extended their work to other chiral species (mainly resolving agents). These workers found that optical rotations of (+)-cinchonine-hydrochloride, (-)-strychninesulphate,(+)-1-quinicacid, (+)-cinchoninemonochlorobromomethylate and (-)-nicotine were markedly altered in presence of certain racemic complexes. These workers observed this effect only in metal complexes of bidentate ligands, 1,10-phenantroline and 2,2 bipyridine. On the other hand a number of metal ions such as Zn^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+} and Mn^{2+} displayed this effect when complexed with these ligands.

Davies and Dwyer[13] observed this effect in $[Cu(phen)_3]^{2+}$ and $[Cu(bipy)_3]^{2+}$ ions in presence of ammonium-d-α-bromo-camphorsulphonate. These workers observed that the rotation was increased with an increase in the concentration of the ligand to a limit of 1:3 metal to ligand ratio. These workers also found that optical rotation of d-tris(ethylenediamine) Co(111) ion is effected in the presence of racemic $[Zn(phen)_3]^{2+}$. This is the first recorded report of optically stable metal complex used to induce the Pfeiffer effect in racemic complexes. Later studies revealved that tris bidentate complexes of Co(III) and Fe(III) with 2,2-bipyridine and 1,10-phenanthroline also showed this effect[14,15] whereas 8-aminoquinoline[16] and ethylenediamine-tetraaceticacid[24] were found to be effective ligands for this purpose. The observed change in rotation with 2,2-dipyridyl complex was very small as compared to that of 1,10-phenanthroline. Pfeiffer postulated that rotational changes of the stable optical species in presence of metal complexes were due to a displacement of equillibrium of a racemic complex. This was later confirmed by Kirschner et.al.[17]

In 1942, Brasted[15] studied this effect and argued that asymmetirc induction could be explained in terms of some sort of bonding between the metal complex and the active environment substance. His work proved that there is some association between the racemic complex and chiral environment compound. Brasted also found that tris 1,10-phenanthroline Co(III) ion is capable of exhibiting this effect. Brasted on the basis of his observation proved that distortion of asymmetric centre due to association was the principal cause of this amomalous effect. The term " Pfeiffer effect" was used for this anomalous change in optical rotation by Dwyer and Brasted in their discussion during a symposium in 1954.

Dwyer and coworkers[18,19] studied this effect and explained it on the basis of an asymmetric electric field from the stable optically active antipode, exerted on the labile metal complex, thereby contributing differentially to the activities of the *dextra* and *leva* metal complex ions. According to this theory an equillibrium shift is subsequently required for the initially racemic complex ion inorder to restore the balanced chemical potential. This is termed as "Configurational activity". A number of observations such as differential increase in solubility of *dextra* and *leva* $[Ru(phen)_3](ClO_4)_3$ in presence of (+)-α-BCS or (+)-tartrate ion supported this theory. It was observed that $(-)$-$[Ru(phen)_3](ClO_4)_3$ in presence of (+)-α-BCS was slightly more soluble in water than its dextro enantionmer.

Similarly $[Ni(bpy)_3]I_2$ could be resolved by recrystallization in presence of ammonium-d-α-bromacamphor-π-sulphonate[20]. Dwyer and Gyarfas were able to isolate a partially resolved sample of $[Co(acac)_3]$ which was allowed to stand in contact with (+)-$[Co(en)_3]I_3$ in an aqueous alcoholic solution. The rates of racemization of *dextro* and *levo* enantioners of $[Ni(bpy)_3]Cl_2$ and $[Ni(phen)_3]I_2$ in presence of chiral environment substance were found to be different in aqueous solution, while no such differences were observed in the presence of $[Co(en)_3]Cl_3$[18,19]. These studies were later questioned by Harris[21] who pointed out that the reactions studied terminate in an equillibrium which did not have the composition of racemic mixture so that the measured velocity coefficient would be expected to be equal if the equillibrium rotation were taken as the end point.

Graddock and Jones[22] studied the hydrolysis of optically active arsenic(v)-catechol complex, $H[As(C_6H_4O)_2]H_2O$ in presence of added asymmetric species. Their results indicated that within the limits of experimental error, added asymmetric species showed no differential effect on the rates of hydrolysis of two enantiomers. These workers repeated the earlier work of Dwyer and coworkers on the rates of racemization of dextro and levo $[Ni(phen)_3]^{2+}$ ions in presence of ammonium-d-α-bromocamphor-π-sulphonate and their results contradicted the previous work.

Ray and Dutt[23] reported a slight difference in rate of racemization of tris-biguanidine Cobalt(III) Chloride d-tartrate and the resolved complex, but later this work was questioned because of changes in the rate caused by temperature.

Kirschner[24] reported the observation of a weak Pfeiffer effect in $[Cu(EDTA)]^{2-}$ complex with L-quinine hydrobromide. On the basis of rotatory dispersion measurements he proved that the Coper(II) ion was six coodinated in this complex.

Landis[16] was unable to observe this effect with $[Zn(EDTA)]^{2-}$ in presence of NH_4-α-BCS. However he observed that zinc complex of 8-aminoquinoline exbibited this effect in presence of the NH_4-α-BCS as environment substance. In this case the active species was not an octahedral tris complex, but a bis(8-aminoquinoline) zinc(II) ion which was optically active due to its tetrahedral configuration. He studied a number of other metal complexes of Zn(II) with the ligands O-phenylenediamine, 1,3-diaminopropanol, dimethylglyoxime, hydroxyquinoline, thioglycolic acid, o-aminobenzoic acid 2-hydroxy pyridine, β-napthoquinoline, acetylacetonate etc, and found that they were unable to induce this effect. Landis[16] also found that Ag(II) and Al(III) when present in solution with both 1,10-phenanthroline and chiral environment substance did not show any change in rotation. In addition the 2,2-bipyridyl and 8-aminoquinoline complexes of Al(III) were also found to be

Pfeiffer inactive. He also studied the Pfeiffer effect in water containing methanol in various molar ratios and found that the effect was quenched with increasing propotions of methanol. This was in accordance with the earlier results reported by Dwyer[25]. Landis also found that addition of ammonia to some Pfeiffer active systems caused a rapid decrease in the effect during the initial addition of ammonia, a gradual decrease in effect thereafter as the concentration of ammonia was increased[16].

Kuhajek[4] in 1962 extensively studied the Zn(II) 1,10-phenanthroline system in presence of a number of chiral environment compounds. He found that temperature concentration of all constituents of the solution and the presence of added salts markedly effect the magnitude of the Pfeiffer effect. He tried to develope optical rotatory dispersion plots for this system using Drude equation, and considering the metal complex as a source of the Pfeiffer effect. He was unable to observe the effect in a solution containing pyridine-2-aldoxime, zinc sulphate and ammonium- d-α-bromo-camphor-π-sulphonate(in 4:1:2 molar ratios).

Nordquist[26] studied the Pfeiffer effect in $[Zn(phen)_3]^{2+}$ with d-α-BCS and d-cinchonine HCl and found that it was appreciably decreased with lowering pH, regardless of the chiral environment compound. The Pfeiffer rotation was also decreased with increasing the temperature of these systems. He attributed the decreased effect due to "Hydrophobic bonding". He further noticed that Pfeiffer effect was appreciably decreased in presence of large amounts of urea. He also studied the effect of isopropanol in these systems, and verified the earlier reports that presence of alcohols quenched the effect.

Kirschner et.al[11] studied the effect on a more quantitative basis and established some numerical expressions to define the the effect. They coined the terms "Pfeiffer rotation" and "Molar Pfeiffer rotation", and reported that these expressions were valid over a wide range of concentrations of environment substance and metal complexes. These expressions are

$$P_\lambda = \pm (\alpha_{e+c} - \alpha_e) \qquad (I)$$

$$[P_M]^t_\lambda = \frac{P_\lambda}{[c][e]xd} \qquad (II)$$

where

P_λ = observed Pfeiffer rotation

α_{e+c} = observed rotation of the environment plus the complex

α_e = observed rotation of the environment only

$[P_M]^t_\lambda$ = Molar Pfeiffer rotation

[c] = Molar concentration of the complex

[e] = Molar concentration of the environment

d = Length of the polarimeter cell in meters

These workers for the first time studied the Pfeiffer effect in non aqueous solvents like DMF and glacial acetic acid.

Doron et.al[27] studied the Pfeiffer effect in some racemic metal complexes of the type$[M(acac)_2Cl_2]$ (M= Sn,Ti) using (+)-tartaric acid as environment substance. They proposed that the Pfeiffer effect was the result of hydrogen bonding of the OH group of tartrate to the halide attached to metal. These workers studied[28] the Pfeiffer effect in some symmetric group(IV) metal halide of the type $[MX_4]$ (where M= Sn, Ti, Zr) in presence of d-malic acid and d-tartaric acid in DMF solution. On the basis of CD spectra they concluded that inner-sphere coordination of the environment was not responsible for the induced optical activity in these systems.

Kan and Brewer[29] studied the Pfeiffer effect in tris oxalato complexes of Al, Fe,Cr,Co and Ir. These workers concluded that source of the Pfeiffer effect in all these systems may be attributed either to an association between complex ion and optically active environment alone(as in case of Ir complex) or to a combination of the association and an equillibrium shift between the two enantiomers in solution.

In 1974 Kirschner et.al[30] studied the Pfeiffer effect in racemic complex $[Co(phen)_3]^{3+}$ using d-malic acid and d-tartaric acid as environment substances. They proposed the enrichment of one enantiomer of the racemic complex due to hydrogen bonding between the environment compound and π-electrons of the aromatic ring system of the ligand. These workers also proposed that hydrogen bonding in optically stable dissymmmetric complexes occured through 'O' atom of the environment compound and proton attached to nitrogen in amine ligand.

Ogino and Kumagai[31] studied the Pfeiffer effect in aqueous solution of $[M(phen)_3]^{2+}$ where ($M = Zn^{2+}$, Ni^{2+}) in presence of various alkaloids. They interpreted their results from the viewpoint of stereoselective association and resulting equillibrium shift and also suggested that the π-π interaction between the complex and the alkaloid conjugate systems contributed to the stereoselective association and hence the Pfeiffer effect. These workers also studied the effect of added electrolyte on Pfeiffer rotation and observed that both sodium chloride and calcium chloride have considerable enhancing effect on Pfeiffer rotation. They assigned Λ absolute configuration to these complexes on the basis of their Pfeiffer rotation.

Kane-Macguire et.al;[32] used the Pfeiffer effect to determine the absolute configuration of D-(+)-$[Co(phen)_3]^{3+}$. The results obtained strongly supported the original 'Λ' assignment to (+)-$[Co(phen)_3]^{3+}$ by Ma son et.al.

Miyoshi and coworkers[33] studied the influence of added salts and lower alcohals on the Pfeiffer effect. Most of the systems showed a linear change in the effect by the added inorganic salts and alcohols like methanol, ethanol and propanol. The added anion reduced the electrostatic repulsion between the complex and the chiral environment compound thereby enhancing the Pfeiffer effect. The added alcohol molecules penetrated into the aggregates composed of complex and chiral cation thereby diminishing the Pfeiffer effect. It was proposed that the complex must come into direct contact with the environment compound inorder to exhibit the Pfeiffer effect. In another study[34] these workers observed that the Pfeiffer effect linearly decreased with the molar concentration of the added alcohol and the logarithm of rate of the decrease in the Pfeiffer rotation is a linear fuction of the CH_2-groups in the added alcohol. This is due to the fact that the added alcohol adheres to the metal complex ion, thereby preventing the chiral acid from coming in direct contact with it.

Miyoshi and coworkers[35,36] also observed that Pfeiffer effect in $[Zn(phen)_3]^{2+}$-strychnine system in water was increased by addition of NH_4Br or $Me_4N^+Br^-$. Addition of $R_4N^+Br^-$ (R= Ethyl, propyl or butyl) did not increase the Pfieffer rotation. These workers also studied inversion in the direction of a chiral equillibrium shift in the Pfeiffer effect of some mixed ligand Cr(III) complexes at the ligand field excited state. Racemic complexes of $[Cr(ox))phen)_2]^+$ and $[Cr(ox)_2(phen)]^-$ were laser irridiated at the ligand field transition region in presence of (+)cinchonine or (-) cinchonidine hydrochloride. These workers observed that a relatively rapid shift in chiral equilibrium in opposite direction occured between these enantiomers and that induced by the usual Pfeiffer effect of the corresponding system in dark. This was in contrast to the observation, that direction of equillibrium shift induced for homochelates $[Cr(ox)_3]^{3-}$ and $[Cr(phen)_3]^{3+}$was unaltered whether they were photo irridiated or not. This was interpreted in terms of anisotropic expansion of these mixed ligands Cr(III) complexes at the ligand field excited state and the accompanying perturbation in their stereoselective interaction with optically active cinchonine or cinchonidine.

Miyoshi and coworkers[37]found a linear relationship between Pfeiffer rotation and concentration of the complex both in H_2O and D_2O and showed that the magnitude of the Pfeiffer rotation was slightly greater in D_2O than in H_2O This was considered as an evidence for hydrophobic bonding.

Hemes[38] studied the mechanism of the Pfeiffer effect in $[Zn(phen)_n](CS)_2$ system by ultrasonic absorption and indicated that there were quick processes in $[Zn(phen)_n](CS)_2$ systems which did not occur for the aquo ion.

Halliday[39]studied the Pfeiffer effect in heterochelates like $[Cr(ox)_2L]^-$ or $[Cr(ox)L_2]^+$ where L= 1,10-phen or 2,2-bpy. They observed that rate of appearance of Pfeiffer activity closely paralleled the rate of racemization. The absolute configuration of the complexes were determined from the relationship between absolute configuration and Pfeiffer effect.

Kirschner et.al[40] studied this effect in tetrahedral complexes with negatively charged complex ions. These workers used racemic mixtures of $[Ni(acac)_2]$ and $[ZnL_2]^{2-}$(L = 8-

hydroxyquinoline-5-sulphate) in presence of (+)-$[Co(en)_3]^{3+}$ as an environment substance.

Brittain and coworkers[41] investigated the Pfeiffer effect in tris(pyridine2,6-dicarboxylato)terbate(III) ion using optically active phenylalkylamine, phenylalkylaminoalcohols and phenylalkylaminoacids as environments and concluded that rotational changes were due to outersphere complexation. They further studied this effect in complexes of Ta(II), Eu(II) and Ho(III) with the same ligand in presence of L-(+)-tartaric acid as environment substance and attributed the rotational changes to outersphere complexation[42].

Kirschner et.al.[43] determined the effect of isotopes in optically labile coordination compounds. Their study provides an evidence in support of equillibrium displacement mechanism for the Pfeiffer effect, and hydrogen bonding mechanism to explain the proposed equillibrium displacement. In particular the effect of replacement of 'H' of the active environment by deuterium iostope. On the Pfeiffer effect is in a manner consistant with the proposed hydrogen bonding between the labile proton of the environment substance and the π-electron cloud of optically labile racemic complexes. These workers also proposed a method for the determination of the absolute configuration of chiral organic acids.

Nomiya and coworkers[44] observed the Pfeiffer effect in a non resolvable enneamolybdomagnate(IV) heteropolyanion

$[MnMo_9O_{32}]^{6-}$ in presence of l-brucine sulphate in organic solvents like acetonitrile and DMF. They studied CD spectra of these systems and assigned Cotton effect bands to various electronic transitions.

Brittain[45] studied the Pfeiffer effect in tris(pyridine, 2,6-dicarboxylato)terbate(III) ion in presence of monosaccharide aldose sugars. He also measured circularly polarized luminescence spectra of these systems and assigned absolute configuration to the complex. He further studied[46] this complex in presence of L-histidine and concluded that hydrogen bonding, hydrophobic and electrostatic effects all contribute to a stronger Pfeiffer effect.

Miyoshi and coworkers[47] studied the Pfeiffer effect in $[Cr(ox)_2phen]^-$ and $[Cr(ox)_2bpy]^-$ complex ions in presence of optically active alkaloids such as (-)-cinchonidine,(-)-quinine and (-)-quinidine. They found that the Pfeiffer effect in these systems was primarily dependent on the configuration around the C-8 and /or C-9 atom of the chiral alkaloid, and their N-1, Me and 9-acetoxy derivatives. They observed that introduction of MeO group at C-6 position on the quinoline ring of each alkaloid lead to a substantial increase in the Pfeiffer effect. While methylation at N-1 diminished the effect. It was further noticed that acetylation of OH group at the C-9 atom shifted the equillibrium greatly in the opposite direction. They obtained the CD and DCD spectra of these systems. Cortes and oworkers[48] studied the discriminating interaction in the Pfeiffer effect in $[Zn(phen)_3]^{2+}$ using l-cystine monohydrochloride as chiral environment substance in aqueous solution.

Hilmes and coworkers[49] studied the quantitative aspects of Pfeiffer effect in dysporium(III) complexes with 2,6-pyridinedicarboxylic acid in aqueous solution. They measured the CD spectra corresponding to certain f-f transitions in solutions containing $[Dy(DPA)_3]^{3-}$ and L-histidine as chiral environment compound. These workers also compared the circularly polarized luminescence spectra before and after the addition of chiral environment compound. Their results supported the equillibrium displacement theory. Similar studies were made by these workers[50] for $[Eu(DPA)_3]^{3-}$ using (+)-dimethyl-L-tartrate as chiral environment substance.

Recently Ahmad and coworkers[51] studied the CD spectra of a number of Pfeiffer effect systems. These workers measured CD spectra of aqueous solutions containing $[M(AA)_2BC]^{n+}$ (where AA is 1,10-phen or bpy and BC is glycinate or pyridine 2-carboxylate ion and M is Co^{2+} or Ni^{2+}) and various chiral environments substances and assigned CD bands to different electronic transitions.

CHAPTER IV

EXPERIMENTAL

1. Materials:

All reagents and solvents were analytical reagent grade and were used without further purification. (+)-α-methylbenzylamine (-)-cinchonidine, $NdCl_3.6H_2O$, $Pr(NO_3)_3.5H_2O$, (+)-tartaric acid, disodiumethylenediaminetetraacetate and diethylenetriaminepentaacetic acid were purchased from Fluka Chemica Switzerland. (+)-cinchonine and 1, 10-phenanthroline were obtained from BDH Chemicals, England, while Ammonium (+)-α-Bromocamphorsulphonate and(-)-10-camphorsulphonic acid were purchased from Aldrich Chemical Company Germany. 2,2-bipyridine was obtained from E. Merk Germany.

2. Preparation of Complexes:

a) $[Cr(phen)_2Cl_2]Cl$ and $[Cr(phen)_2ox]Cl$ were prepared by literature methods[52]. Similarly reported methods were used for the preparation of $K_3[Cr(malon)_3]$[55], $Na_2[Cr(DTPA)]$[54], $[Co(BPA)_3](ClO_4)_2$[56] and $[Ni(BPA)_3](ClO_4)_2$[57].

b) $[Cr(bipy)_2(gly)]Cl_2$ was prepared by the method of Broomhead[52] with slight modification as given below.

In a round bottom flask 0.01 mole of $CrCl_3.6H_2O$ was dissolved in 50 ml of methanol with stirring. A single piece of mossy zinc was placed in the flask. Then two solutions one containing 0.02 mole of 2,2-bipy in methonal and the other containing 0.01 mole of sodium glycinate in water were added to the reaction solution. The reaction mixture was slowly brought to reflux and kept as such for one hour. During refluxing colour of the reaction mixture was changed to red brown. The reaction mixture was then concentrated on a water bath and kept over night at room temperature. The crystals were filtered through a glass frit of medium porosity, washed with methanol and air dried. The crystalline product was analyzed

Analytical: For $[Cr(C_{20}H_{12}N_5O_2)]Cl_2$.

Calculated:	C 51.87	H 3.93	N 13.17	Cr	10.21%
Found:	C 52.13	H 3.82	N 12.83	Cr	9.88%

c) Preparation of $[Cr(bipy)_2(H_2O)_2]Cl_3$

Sysnthesis of $[Cr(bipy)_2(pyca)]Cl_2$ was attempted by mixing appropriate amounts of $CrCl_3.6H_2O$, 2,2-bipyridine and pyridine 2-carboxylic acid in methanol and refluxing as given above. However analysis of the crystalized complex indicated it as $[Cr(bipy)_2(H_2O)_2]Cl_3$.

Analysis: For $[Cr(C_{10}H_8N_2)_2(H_2O)_2]Cl_3$.

Calculated:	C 46.57	H 4.07	N 20.62	Cr	10.08%
Found:	C 46.46	H 3.59	N 20.10	Cr	10.20%

d) Preparation of $Na[Cr(EDTA)H_2O]$

This complex was prepared by literature method[53]. The product obtained was in the form of viscous liquid. However the complex was crystallized out from the viscous liquid by slowly adding excess of absolute ethanol with vigorous stirring. The complex is hygroscopic and must be stored in a vacuum dessicator.

e) Preparation of $[Cu(2\text{-picolylamine})_2](ClO_4)_2$

It was prepared by mixing hot methanol solutions of appropriate amounts of Copper(II) perchlorate hexahydrate (0.01 mole) and 2-picolylamine (0.03 mole) in a round bottom flask. The complex crystallized out as violet needles upon cooling the reaction mixture. The complex was filtered through a glass frit and washed with methanol inorder to remove the excess ligand.

Analytical: For $[Cu(C_{12}H_{16}N_4)](ClO_4)_2$.

Calculated:	C 30.10	H 3.37	N 11.70	Cu	13.27%
Found:	C 30.29	H 3.30	N 11.74	Cu	13.15%

f) Preparation of $[V(phen)_2Cl_2]Cl$ and $[V(bipy)_2Cl_2]Cl$

These were prepared in methanol under inert atmosphere as follow:

In a two neck round bottom flask 0.01 mole of VCl_3 was dissolved in 50 ml of methanol. The flask was flushed with dry nitrogen gas to remove air. Then methanol solution of

0.03 mole of 2,2-bipy / 1,10-phen were added to the metal ion solution. The reaction mixture was brought to reflux and stirred under a continuous flow of N_2. The colour of the reaction mixture immediately turned to dark purple. After about 15 minutes the reaction mixture was cooled in ice, when dark purple crystalline complexes separated out. The complexes were filtered and washed with methanol. It has been reported that these complexes formed dimeric hydroxo bridged species like $[(AA)_2V(\mu\text{-}OH)_2V(AA)_2]^{4+}$(where AA= 2,2-bipy or 1,10-phen) upon dissolution in water[59]. The absorption spectra of aqueous solution of these complexes are similar to those reported in the literature[59].

g) Preparation of $NH_4[Nd(EDTA)]$ and $NH_4[Pr(EDTA)]$

These complexes were prepared by a reported method[60] with slight modification as given below.

0.2 moles of neodymium chloride hexahydrate were dissolved in 50 ml of water. Another solution containing the same molar quantity of $(NH_4)_2H_2EDTA$ was prepared by titrating the free acid with NH_4OH until pH of the solution reached to 8. The two solutions were mixed and stirred for 10-15 minutes. The reaction mixture was concentrated on water bath and then cooled. The cooled reaction mixture was added drop by drop to an excess of ethanol with vigorous stirring. The solid complexes were seperated out. These complexes were filtered on a glass frit, washed with water and then dried in oven at 110°C.

3. Preparation of solutions for CD studies:

a) Stock solutions of optically active environment substances like (-)-malic acid (+)-tartaric acid, (+)-ascorbic acid were prepared by dissolving appropriate amounts (0.04 mole) in small volumes of doubly distilled water and diluting to 100 ml in volumetric flasks. The solutions were thoroughly mixed and kept in dark.

b) The optically active environment compounds (+)-cinchonine, (-)-cinchonidine, (+)-α-methylbenzylamine, (-)-quinine and (-)-brucine are insoluble in water. Therefore these compounds were converted into their hydrochlorides as given below.

Accurately weighed quantities of the environment compound were dissolved in minimum amount of dil HCl. The solutions were concentrated on a water bath. The solutions were cooled in an ice bath when hydrochloride salts of the environment compounds were seperated as fine crystalline material. The crystals were filtered, washed with water and then dried. Calculated amounts of crystalline hydrochloride salts of these chiral environment substances were dissolved in water and diluted to mark in volumetric flasks. These solutions were thoroughly mixed and kept in dark.

c) In certain cases stock solutions of the insoluble environment compounds were prepared by dissolving calculated amounts of the solid subtances in minimum volume of dil HCl and diluting with distilled water to 100 ml in volumetric flasks. The solutions were thoroughly mixed and kept in dark.

d) Preparation of solutions for the Pfeiffer effect studies: Calculated amounts of the metal complexes were dissolved in a small volume of the stock solution of the environment substance and then transfered to a 25 ml volumetric flask. These were diluted to the mark with the stock solution of the environment substances. The contents were thoroughly mixed and kept in dark for 1-2 hours before measuring their CD spectra.

e) Preparation of solutions of complexes in perchlorate form: The water insoluble complexes like $[Co(BPA)_3](ClO_4)_2$, $[Cu(ampy)_2](ClO_4)_2$, $[(phen)_2V(\mu\text{-}OH)_2V(phen)_2](ClO_4)_4$ were converted to soluble chloride form before their use in the Pfeiffer effect studies. Aqueous solutions of these complexes were obtained as given below.

0.001 mole of each complex was moistened with water and brought in contact with 5-10 grams of strongly acidic anion exchange resin (Amberlite IRA-400) in chloride form. The mixture was stirred for a few minutes untill a clear solution of the complex was obtained. The resin was then filtered off. To the filterate calculated amounts of the solid environment substances were added and diluted to the mark in volumetric flasks. These solutions were thorougly mixed and kept in dark for 1-2 hours before recording their CD spectra.

f) Preparation of $[V(EDTA)]^-$ and $[V(DTPA)]^{2-}$ for Pfeiffer CD studies.

Aqeous solutions (0.1M) of these complexes were prepared by dissolving calculated amount of VCl_3(0.01 moles) in about 50 ml of water and adding 0.01 mole of EDTA or DTPA disodium salt with stirring. The resulting brown solutions were diluted to 100 ml in volumetric flasks and thoroughly mixed. Then calculated amount of the solid environment substances were dissolved in about 20 ml of the complex ion solution and transferred to 25 ml volumetric flasks. The solutions were diluted to the mark with complex ion solution and thoroughly mixed. The final concentrations of the complex and environment substances were maintained at 0.1M and 0.3M respectively.

g) Preparation of solutions of $[Nd(EDTA)]^-$ for CD studies.

0.2M solution of $NH_4[Nd(EDTA)]$ was prepared in a 25 ml volumetric flask. To each of five volumetric flasks of 10 ml capacity were added 5 ml of the metal complex ion solution. Calculated amount of (+)-T·A was added to each flask and determined its pH which was found as 2.The pH of these solutions were adjusted at 2, 4, 6, 8, 10 with dilute solution of NaOH. The volume of each flask was then adjusted to the mark with distilled water.

4. Instrumentation:

Elemental analysis were obtained from Midwest Microlab, Indianapolis, U.S.A. Melting points were determined on Thomas Hoover unimelt apparatus obtained from Arther Thomas Company Philadelphia, P.A, U.S.A. Metal contents of these complexes were determined on Shimadzo Model 670AA, atomic absorption spectrophotometer. The I.R spectra of the solid complexes in KBr disc were recorded on Hitachi Model 250-70 spectrophotometer.

The absorption spectra of solutions of these complexes in 400-700 nm range were recorded on Hitachi Model 220S recording spectrophotometer. A matched pair of quartz cells of 10 mm thickness were used for these measurements and $1x10^{-2}-10^{-3}M$ concentations of complexes were used. pH measurements of these solutions were carried out on a digital pH meter Horiba model F-8 equipped with a glass and calomel reference electrode.

The CD spectra of aqueous solutions of these Pfeiffer systems in the wavelength range 400-700nm were recorded on JASCO-20A spectropolarimeter. This instrument uses Xenon Arc lamp as a light source and is equipped with a recorder. Special strain free quartz cells of 1-10mm thickness were used. Aqueous solutions of the chiral environment copmounds were used to record base line of these spectra as the environment compounds are colourless and have no CD bands in visible region of the spectra.

CHAPTER V

(a) INVESTIGATION OF NEW PFEIFFER ACTIVE SYSTEMS:

Pfeiffer effect was studied in a number of racemic complexes in presence of some new environment compounds. Examination of previous studies on the Pfeiffer effect indicate that only octahedral complexes of 1,10-phenanthroline, 2,2-bipyridyl and oxalate ion are capable of showing this effect. To date there has been only one tetrahedral complex i.e. bis(8-aminoquinoline) Zn(II) ion which shows this effect. Further a limited number of chiral environment substances such as NH_4-α-BCS, d-10-camphorsulphonic acid, d and l enantiomers of tartaric acid and malic acid may be used for inducing this effect. However a few complexes of other ligands such as $[Cu(EDTA)]^{2-}$,$[Zn(8\text{-amq})2]^{2+}$ $[Zn(pyim)_3]$,$[Al(hfa)_3]$ and $[Ni(BBMI)_3]^{2+}$ in presence of certain common chiral environment substances also show this effect.

There are two features common in most of the Pfeiffer active systems, i.e. the metal ions belong to the labile group of metals and the ligands in these complexes have appreciable pi bonding. There have been reports that metal complexes of saturated ligands such as $[Zn(en)_3]^{2+}$, $Ni(en)_3]^{2+}$ and $[Co(en)_3]^{2+}$donot show the Pfeiffer effect in presence of any chiral environment compound. In order to substantiate this observation a large number of complexes of other ligands with appreciable pi bonding have been synthesized for the Pfeiffer effect studies. In particular complexes of ligands such as picolinic acid (pyca), bipyridylamine (BPA) and 2-aminomethylpyridine which have nitrogen donor atoms in pyridine rings at appropriate positions for bidentate chelation were studied for the Pfeiffer effect in presence of various chiral environment substances. A number of complexes like $[Cr(pyca)_3]$, $[Co(BPA)_3](ClO_4)_2$, $[Ni(BPA)_3](ClO_4)_2$ and $[Cu(BPA)_3](ClO_4)_2$ were prepared by literature methods. Attempts were made to synthesise tris complexes of Co^{2+}, Ni^{2+}, Cu^{2+} with 2-(aminomethyl)pyridine (another bidentate ligand of pyridine origin) for the Pfeiffer effect studies. However only bis complexes of 2-(aminomethyl) pyridine with these metal ions were the only products isolated from the reaction mixture. The Pfeiffer effect was not induced in solutions of $[Co(ampy)_2]^{2+}$ and $[Ni(ampy)_2]^{2+}$ in presence of various environment substances. However $[Cu(ampy)_2]^{2+}$ showed small changes in optical rotation in presence of NH_4-(+)-α-BCS and NH_4(-)-10-CSA. Since this type of bis complexes in square planar environment should be symmetrical, they are not expected to show the Pefiffer effect. It may be assumed that the complex $[Cu(2\text{-}ampy)_2]^{2+}$ ion has either a distorted tetrahedral environment around the metal ion or two solvent molcules have occupied cis position in the coordination sphere of the metal ion, forming dissymmetric cis-$[Cu(ampy)_2(H_2O)_2]^{2+}$. The later possibility seems more probable due to appearance of CD bands in visible region of the spectrum.

A series of complex ions like $[Co(BPA)_3]^{2+}$, $[Ni(BPA)_3]^{2+}$ and $[Cu(BPA)_3]^{2+}$ were investigated for the Pfeiffer effect in presence of various environment substances. The Pfeiffer effect was induced only in $[Co(BPA)_3]^{2+}$ in presence of (-)-10-camphorsulphonic acid and ammonium (+)-α-bromocamphor-π-sulphonate. The optical rotation changes were very small in these systems(Table I). It is commonly observed that specific rotations of tris type complexes of different metal ions with bipyridyl ligands are relatively smaller as compared to those of 1,10-phenanthroline ligands e.g; $[Fe(phen)_3]^{2+}$, $[Fe(bpy)_3]^{2+}$ and $[Ni(phen)_3]^{2+}$, $[Ni(bpy)_3]^{2+}$. Similarly values of Pfeiffer rotations in $[Ni(phen)_3]^{2+}$ in presence of (+)-ammonium-α-bromocamphorsulphonate and other environments are very large as compared to those in $[Ni(bpy)_3]^{2+}$ ion. The magnitude of molar Pfeiffer rotation seems to depend upon the structure of the ligand i.e; 1,10-phenanthroline being a three six membered fused ring system induce larger rotations as compared to bipridyl consisting of only two relatively free rotating pyridine rings. If this argument is acceptable then bipyridylamine is rather more flexible molecule, and its complexes shold have lower specific and molar Pfeiffer rotations. This is demonstrated by analogous complexes of Mn,$^{2+}$, Co^{2+}, Ni^{2+}, and Cu^{2+}. It is also evident from the fact that

Table-I The Pfeiffer Effect in Cobalt(II) and Copper(II) Complex Ions in Presence of Various Chiral Environment Substances in Aqueous Solution.

Complex Ion (0.03M)	Environment Compound (0.12M)	P_{obs}	$[P_M]^{25}_{589}$
$[Co(BPA)_3]^{2+}$	(-)-10-Camphorsulphonic Acid	0.006	166.6
$[Co(BPA)_3]^{2+}$	NH_4-α-Bromocamphorsulphonate	0.02	555.5
$[Cu(ampy)_2]^{2+}$	(-)-10-Camphorsulphonic Acid	0.02	555.5
$[Cu(ampy)_2]^{2+}$	NH_4-α-Bromocamphorsulphonate	0.02	555.5

$[Co(phen)_3]^{2+}$ ion in presence of (-)-malic acid has molar Pfeiffer rotation of 2575 degrees while $[Co(BPA)_3]^{2+}$ in presence of this environment substance has only 167 degrees.

$[Cu(EDTA)]^{2-}$ is the only example of sexadentate $EDTA^{4-}$ ligand showing this effect in presence of l-quinine hydrobromide. In this complex pi bonding in acetate group which is a part of the chelate, may be responsible for inducing the Pfeiffer effect. A number of complexes of $EDTA^{4-}$ and another polycarboxylate ion $DTPA^{5-}$ were synthesized for exploring their Pfeiffer activity. The Pfeiffer effect was studied in complexes of the metal ions Fe^{3+}, Ni^{2+}, Cu^{2+}, Cr^{3+} and V^{3+} in presence of reported and new chiral environment substances. It is apparant from Table II that very little or no changes in rotation were observed in most of these systems. However a few complexes like $[Cr(EDTA)H_2O]^-$, $[Cr(DTPA)]^{2-}$, $[V(EDTA)]^-$, $[V(DTPA)]^{2-}$ showed small rotational changes in presence of various environment compounds. The molar Pfeiffer rotation for these systems are given in Table III. A positive Pfeiffer effect was observed in complexes $[Cr(EDTA)H_2O]^-$ and $[Cr\ (DTPA)]^{2-}$ in presence of all the enviornment compounds while $[V(EDTA)]^-$ showed a negative Pfeiffer effect in presence of (+)-cinchonine HCl, (-)-cinchonidine HCl, (-)-brucine HCl (+) tartaric acid and (-)-tartaric acid. This complex exhibited a positive Pfeiffer effect in presence of (+)-α-methylbenzylamine HCl and (-)-ephedrine HCl. $[V(DTPA)]^{2-}$ showed positive Pfeiffer effect in

Table-II Complex Ions and Environment Substances Which do not Show the Pfeiffer Effect.

Complex	Environment Compound
$[Cr(EDTA)H_2O]^-$	(-) - Brucine.HCl
$[Cr(EDTA)H_2O]^-$	(-) - Quinine.HCl
$[Cr(EDTA)H_2O]^-$	(+) - Arabinose
$[Cr(EDTA)H_2O]^-$	(+) - α-Methylbenzylamine.HCl
$[Cr(DTPA)]^{2-}$	(+) - Cinchonine.HCl
$[Cr(DTPA)]^{2-}$	(-) - Cinchonidine.HCl
$[Cr(DTPA)]^{2-}$	(-) - Quinine.HCl
$[Cr(DTPA)]^{2-}$	(-) - Brucine.HCl
$[Cr(DTPA)]^{2-}$	(+) - Arabinose
$[Cr(DTPA)]^{2-}$	(+) - α-Methylbenzylamine.HCl
$[Cr(phen)_2Cl_2]^+$	(-) - Quinine.HCl
$[Cr(phen)_2Cl_2]^+$	(-) - Brucine.HCl
$[Cr(phen)_2Cl_2]^+$	(+) - Arabinose
$[Cr(phen)_2Cl_2]^+$	(+) - Ascorbic Acid
$[Cr(phen)_2Cl_2]^+$	(+) - α-Methylbenzylamine.HCl
$[Cr(phen)_2Cl_2]^+$	NH_4 - (+) - α-BCS
$[Cr(bpy)_2gly]^{2+}$	NH_4 - (+) - α-BCS
$[Cr(bpy)_2gly]^{2+}$	(-) - 10-Camphorsulphonic Acid
$[Cr(bpy)_2gly]^{2+}$	(-) - Brucine.HCl
$[Cr(bpy)_2gly]^{2+}$	(-) - Quinine.HCl
$[Cr(bpy)_2gly]^{2+}$	(+) - α-Methylbenzylamine.HCl

Contd.

Complex	Environment Compound
$[Cr(bpy)_2gly]^{2+}$	(+) - Arabinose
Cis-$[Cr(bpy)_2(H_2O)_2]^{3+}$	NH_4 - (+) - α-BCS
Cis-$[Cr(bpy)_2(H_2O)_2]^{3+}$	(-) - 10-Camphorsulphonic Acid
Cis-$[Cr(bpy)_2(H_2O)_2]^{3+}$	(-) - Brucine.HCl
Cis-$[Cr(bpy)_2(H_2O)_2]^{3+}$	(-) - Quinine.HCl
Cis-$[Cr(bpy)_2(H_2O)_2]^{3+}$	(+) - α-Methylbenzylamine.HCl
Cis-$[Cr(bpy)_2(H_2O)_2]^{3+}$	(+) - Arabinose
$[Co(EDTA)]^{-}$	(+) - Cinchonine.HCl
$[Co(EDTA)]^{-}$	(-) - Quinine.HCl
$[Co(EDTA)]^{-}$	(+) - Tartaric Acid
$[Co(EDTA)]^{-}$	(+) - α-Methylbenzylamine.HCl
$[Co(BPA)_3]^{2+}$	(+) - Cinchonine.HCl
$[Co(BPA)_3]^{2+}$	(-) - Cinchonidine.HCl
$[Co(BPA)_3]^{2+}$	(+) - Tartaric Acid
$[Co(BPA)_3]^{2+}$	(+) - Pantothenic Acid
$[Co(BPA)_3]^{2+}$	(+) - Ascorbic Acid
$[Ni(EDTA)]^{2-}$	(+) - Cinchonine.HCl
$[Ni(EDTA)]^{2-}$	(-) - Cinchonidine.HCl
$[Ni(EDTA)]^{2-}$	(+) - Tartaric Acid
$[Ni(EDTA)]^{2-}$	(+) - Pantothenic Acid
$[Ni(EDTA)]^{2-}$	(+) - Ascorbic Acid
$[Ni(BPA)_3]^{2+}$	(+) - Cinchonine.HCl
$[Ni(BPA)_3]^{2+}$	(-) - Cinchonidine.HCl

Contd.

Complex	Environment Compound
$[Ni(BPA)_3]^{2+}$	(+) - Tartaric Acid
$[Ni(BPA)_3]^{2+}$	(+) - Pantothenic Acid
$[Ni(BPA)_3]^{2+}$	(+) - Ascorbic Acid
$[Cu(BPA)_3]^{2+}$	(+) - Tartaric Acid
$[Cu(BPA)_3]^{2+}$	(+) - Cinchonine.HCl
$[Cu(BPA)_3]^{2+}$	(-) - Cinchonidine.HCl
$[Cu(BPA)_3]^{2+}$	(-) - Quinine.HCl
$[Cu(BPA)_3]^{2+}$	(-) - Brucine.HCl
$[Cu(BPA)_3]^{2+}$	(+) - Arabinose
$[Cu(phen)_3]^{2+}$	(+) - Tartaric Acid
$[Cu(phen)_3]^{2+}$	(+) - Cinchonine.HCl
$[Cu(phen)_3]^{2+}$	(-) - Cinchonidine.HCl
$[Cu(phen)_3]^{2+}$	(-) - Quinine.HCl
$[Cu(phen)_3]^{2+}$	(-) - Brucine.HCl
$[Cu(phen)_3]^{2+}$	(+) - Arabinose
$[Cu(bpy)_3]^{2+}$	(+) - Tartaric Acid
$[Cu(bpy)_3]^{2+}$	(+) - Cinchonine.HCl
$[Cu(bpy)_3]^{2+}$	(-) - Cinchonidine.HCl
$[Cu(bpy)_3]^{2+}$	(-) - Quinine.HCl
$[Cu(bpy)_3]^{2+}$	(-) - Brucine.HCl
$[Cu(bpy)_3]^{2+}$	(+) - Arabinose
$[Cu(ampy)_2]^{2+}$	(+) - Cinchonine.HCl
$[Cu(ampy)_2]^{2+}$	(-) - Cinchonidine.HCl

Contd.

Complex	Environment Compound
$[Cu(ampy)_2]^{2+}$	(-) - Quinine.HCl
$[Cu(ampy)_2]^{2+}$	(+) - Tartaric Acid
$[Cu(ampy)_2]^{2+}$	(+) - Ascorbic Acid
$[Pr(EDTA)]^{-}$	(+) - Tartaric Acid
$[Pr(EDTA)]^{-}$	(-) - Cinchonidine.HCl
$[Pr(EDTA)]^{-}$	(+) - Cinchonine.HCl
$[Pr(EDTA)]^{-}$	(-) - Histidine
$[Nd(EDTA)]^{-}$	(-) - Histidine

presence of (+)-α-methylbenzylamine HCl and negative Pfeiffer effect in presence of (-)-cinchonidine HCl and (+)-cinchonine HCl. The results are given in Table IV.

As stated earlier, most of the Pfeiffer effect studies have been carried out on complexes of labile metal ions. However tris oxalato complexes of two inert metal ions like Co^{3+} and Cr^{3+} also show this effect in presence of (+)-cinchonine HCl. The resolved complex $K_3[Cr(ox)_3]$ rapidly racemizes in solution. A number of mixed ligand complexes of Cr^{3+} with 2,2-bipy and 1,10-phen have been reported in the past. The ambidentate, anion or water in complexes like $[Cr(AA)_2X_2]^{n+}$ (When AA=2,2-bipy or 1,10-phen and X = Cl^-, Br^-, H_2O) commonly assume a cis position and exist as 'd' and 'l' enantiomers. The enantiomeric forms of these complexes are expected to racemize at a faster rate. Therefore a series of mixed ligand chromium(III) complexes like $[Cr(AA)_2X_2]Cl$ alongwith $K_3[Cr(malon)_3]$ were prepared and investigated for the Pfeiffer effect in presence of various environment compounds. The results are reported in Table V. It is apparant from the table that all these complexes show a negative Pfeiffer effect in presence of (+)-cinchonine HCl and (-)-cinchonidine HCl. Two other complexes $[Cr(bpy)_2 Cl_2]Cl$ and $[Cr(bpy)_2gly]Cl_2$ show a positive Pfeiffer effect in presence of (+)-tartaric acid, indicating that dextro enantiomers of these complexes are enriched. $[Cr(bpy)_2ox]Cl$ shows a negative Pfeiffer effect in

Table-III Molar Pfeiffer Rotations of the Pfeiffer Systems Containing the Chromium(III) Complexes of Polyamine Carboxylic Acids and Various Environment Substances in Aqueous Solution.

Complex(0.025M)	Environment Compound(0.1M)	P_{obs}	$[P_M]^{25}_{589}$
$Na[Cr(EDTA)H_2O]$	(+) - Cinchonine.HCl	0.04	1600
$Na[Cr(EDTA)H_2O]$	(-) - Cinchonidine.HCl	0.04	1600
$Na[Cr(EDTA)H_2O]$	(+) - Ascorbic Acid	0.001	40
$Na[Cr(EDTA)H_2O]$	(+) - Tartaric Acid	0.001	40
$Na[Cr(EDTA)H_2O]$	(-) - Tartaric Acid	0.001	40
$Na_2[Cr(DTPA)]$	(+) - α-MBA.HCl	0.001	40
$Na_2[Cr(DTPA)]$	(+) - Tartaric Acid	0.006	240
$Na_2[Cr(DTPA)]$	(+) - Ascorbic Acid	0.002	80

Table-IV Pfeiffer Effect in $[V(EDTA)]^-$ and $[V(DTPA)]^{2-}$ in Presence of Various Chiral Environment Substances in Aqueous Solution.

Complex	[Conc.]	Environment	[Conc.]	P_{obs}	$[P_M]^{25}_{589}$
$[V(EDTA)]^-$	0.1	(-)-Cinchonidine.HCl	0.3	-0.4	-1333
$[V(EDTA)]^-$	0.1	(+)-α-MBA.HCl	0.3	0.05	166.6
$[V(EDTA)]^-$	0.1	(+)-Tartaric Acid	0.3	0.06	200
$[V(EDTA)]^-$	0.1	(-)-Tartaric Acid	0.3	0.06	200
$[V(EDTA)]^-$	0.05	(-)-Brucine.HCl	0.075	-0.2	-5333
$[V(EDTA)]^-$	0.04	(-)-Ephedrine.HCl	0.12	0.01	208.3
$[V(DTPA)]^{2-}$	0.1	(-)-Cinchonidine.HCl	0.3	-0.06	-200
$[V(DTPA)]^{2-}$	0.1	(+)-α-MBA.HCl	0.3	0.54	180.6

Table-V Pfeiffer Effect in Mixed Ligand Complexes of Cr(III) in Presence of Various Chiral Environment Substances in Water Solutions.

Complex	Environment Substance	P_{obs}	$[P_M]_{589}^{25}$
$[Cr(phen)_2Cl_2]Cl$ (0.025M)	(+)-Cinch.HCl (0.15M)	-0.015	-400
	(-)-Cinchd.HCl (0.15M)	-0.015	-400
$[Cr(bpy)_2Cl_2]Cl$ (0.025M)	(+)-Cinch.HCl (0.75M)	-0.015	-800
	(-)-Cinchd.HCl (0.75M)	-0.015	-800
	(+)-T.A. (0.1M)	+0.006	+240
$[Cr(bpy)_2(H_2O)_2]Cl_3$ (0.04M)	(+)-Cinch.HCl (0.12M)	-0.019	-400
	(-)-Cinchd.HCl (0.12M)	-0.019	-400
$[Cr(bpy)_2gly]Cl_2$ (0.025M)	(+)-Cinch.HCl (0.20M)	-0.06	-1200
	(-)-Cinchd.HCl (0.20M)	-0.06	-1200
	(+)-T.A. (0.20M)	+0.093	+1875
$[Cr(phen)_2ox]Cl$ (0.025M)	(+)-Cinch.HCl (0.08M)	-0.004	-240
	(-)-Cinchd.HCl (0.08M)	-0.004	-240

presence of (+)-cinchonine HCl and (-)-cinchonidine HCl in aqueous solution.

In aqueous solutions $K_3[Cr(malon)_3]$ whows a positive Pfeiffer effect in presence of (-)-cinchonidine HCl, (+)-α-methylbenzylamine HCl and (-)-ephedrine HCl, while a negative Pfeiffer effect is observed in presence of (-)-quinine HCl. It is revealed that *levo* enantiomer of $[Cr(malon)_3]^{3-}$ is enriched in presence of (-)-cinchonidine HCl, (-)-ephedrine HCl and (-)-brucine HCl while *dextro* enantiomer is enriched in presence of (+)-α-methylbenzylamine HCl and (-)-quinine HCl. The induced Pfeiffer effect decrease in the order (-)-brucine HCl > (-)-cinchonidine HCl > (-)-ephedrinein HCl > (+)-α-methylbenzylamine HCl > (-)-quinine HCl in these systems (Table VI).

The Pfeiffer effect in complexes of lanthanide metal ions such as $[Dy(DPA)_3]^{3-}$ and $[Eu(DPA)_3]^{3-}$ have been reported recently.[49,50] However further studies on complexes of f-block elements are needed. Therefore complexes of metal ions like Nd^{3+} and Pr^{3+} with polycarboxylate anions such as $EDTA^{4-}$ and $DTPA^{5-}$ were prepared in solution as well as in solid form by literature methods. These complexes were investigated for their Pfeiffer effect in presence of various environment compounds. Only $(Nd(EDTA)]^-$ ion showed a small increase in rotation of (-)-cinchonidine HCl and a small decrease in rotation of (+)-tartaric acid. The change in rotation is dependent upon concentration of the components and also depends upon pH of the

Table-VI The Pfeiffer Effect in $K_3[Cr(malon)_3]$ (0.03M) in Presence of Various Environment Substances in Aqueous Solution.

Environment Compound	[Conc.]	P_{obs}	$[P_M]_{589}^{25}$
(+)-α-MBA.HCl	0.24	0.008	111.1
(−)-Cinchonidine.HCl	0.12	0.05	1388
(−)-Brucine.HCl	0.12	0.75	2083
(−) - Quinine.HCl	0.10	−0.01	−333.3
(−)-Ephedrine.HCl	0.12	0.005	138.8

system. At lower pH values, the Pfeiffer effect is quenched.

The Pfeiffer effect in $K_3[V(C_2O_4)_3]$ in presence of (+)-cinchonine HCl was reported in 1969[62]. Although a number of octahederal vanadium (III) complexes such as $[V(AA)_2X_2]X$ (AA=2,2-bipy or 1,10-phen $X=Br^- Cl^-$) have been reported in the literature, Pfeiffer effect studies on such complexes have never been carried out. When aqueous solutions of V(III) and the ligands (bipy or phen) in 1:3 molar ratios were mixed under N_2 atmosphere, deep purple complex ions were formed. These complexes have been assigned a dimeric $[V_2(OH)_2(phen)_4]^{4+}$structure by earlier workers.[77] The sulphate and perchlorate salts of this deep purple complex are sparingly soluble in water and quite stable in air. However aqueous solutions of these complexes are slowly oxidized to tetravalent vanadyl complexes. A purple crystalline product $[V(phen)_2Cl_2]Cl$ may be obtained by reacting appropriate amounts of metal chlorid and ligands from non aqueous solvents such as methanol or by fusion of VCl_3 with solid 1,10-phenanthroline, which is easily hydrolyzed to hydroxo complex in aqueous solution. Later worker confirmed binuclear structure with hydroxobridges for these complexes[59,61]. The two complex ions $[V_2(phen)_4(\mu\text{-}OH)2]^{4+}$and $[V_2(bipy)_4(\mu\text{-}OH)_2]^{4+}$ were prepared and studied for their Pfeiffer activity in presence of a number of environment substances like (-)-malic acid, (÷)-tartaric acid, (+)-ascorbic acid, (-)-cinchonidine HCl and (+)-α-methylbenzylamine HCl. These complexes show small optical rotational changes in presence of (+)-ascorbic acid. However large rotational changes were observed in presence of (-)-malic acid, (+) and (-)-tartaric acid, indicating that some interaction between the complex and environment substance had occured. Examination of Circular Dichroism spectra of these complexes in presence of various environment compounds indicated an asymmentric synthesis of binuclear species in solution.

(b) INVESTIGATION OF NEW ENVIRONMENT SUBSTANCES:

Todate only a limited number of chiral environment compounds have been effectively used for inducing the Pfeiffer effect in racemic complexes. In the present work efforts were made to explore new chiral environment substances which may induce the Pfeiffer effect. For this purpose a number of new optically active organic compounds like (+)-α-methylbenzylamine HCl, (-)-quinine HCl, (-)-brucine HCl, (+)-ascorbic acid, (+)-arabinose, (+)-usnic acid, (-)-thiazolidine carboxylic acid, (+)-sodiumpantothenate and (-)-cinchonidine HCl were studied in presence of a number of dissymmetric complexes including the above mentioned Pfeiffer active complexes. It was found that only (+)-α-methylbenzylamine HCl, and (-)-cinchonidine HCl induced Pfeiffer activity in complexes $[Cr(DTPA)]^{2-}$, $[Cr(malon)_3]^{3-}$,$[V(EDTA)]^-$ and $[V(DTPA)]^{2-}$ in aqueous solutions. (-)-Ephedrine HCl and (-)-brucine HCl were found as effective environment substances for $[Cr(malon)_3]^{3-}$,$[V(EDTA)]^-$ complex ions while (-)-quinine HCl showed Pfeiffer effect only with $[Cr(malon)_3]^{3-}$.

It is interesting to pointout that two alkaloid bases like (-)-cinchonine and (-)-quinine have very similar molecular structure, accept that quinine has a methoxy substituent at '7' position in quinoline ring. However (-)-cinchonidine and (+)-cinchonine are very effective environment substances for inducing the Pfeiffer effect in a number of racemic complexes, while (-)-quinine and its enantiomer (+)-quinidine does not induce this effect in most of the complexes studied. This difference in activity of these two environment substances seems to arise from effective shielding of propellor of asymmetric carbon atom in these chiral environments, restricting an effective and preferred interaction with the dissymmetric complexes.

CHAPTER VI

CIRCULAR DICHROISM STUDIES OF PFEIFFER EFFECT SYSTEMS

The racemic metal complexes and chiral environment substances in the Pfeiffer systems normally absorb in different spectral regions. The environment substances and the ligands involved in these chelates commonly absorb in ultraviolet region, while metal complexes have absorption bands in visible as well as in ultraviolet region of the spectrum. The absorption bands in UV region are due to allowed electronic transitions and therefore are very intense (i.e extinction coefficients of such bands are very high). Absorption bands due to d-d transitions are observed in visible region of the spectrum and are associated with lower values of extinction coefficient. It has been demonstrated by earlier workers that the Pfeiffer effect systems show CD bands in visible region where neither ligands nor chiral environment compounds have any absorption. This was presented as an evidence in favour of "displacement in equillibrium" concept of the Pfeiffer effect. Therefore CD spectra of all those complexes showing the Pfeiffer effect were studied.

This technique has certain limitations that CD bands due to charge transfer transitions of complexes cannot be observed because of very strong bands of the environment substances present in high concentrations in these systems. However CD bands of these systems in visible region may be interpreted in terms of electronic transitions within d orbitals, and absolute configuration of the ligands around the metal ion may be deter mined

a) Study of Mixed Ligand Complexes of Chromium (III):

The absorption spectra of these complexes in presence of various environment substances were indentical to those taken for the aqueous solutions of these complexes. This indicated that no appreciable interaction between the complexes and the environment substances occured. The band positions and molar extinction coefficients of these complexes are reported in table VII The absorption spectra of these complexes invariably consist of a single band between 18,867 cm^{-1} to 20,202 cm^{-1} with extinction coefficient values between 42-112 $M^{-1}cm^{-1}$.

CD sepctra of cis-$[Cr(phen)_2Cl_2]^+$, cis-$[Cr(bpy)_2Cl_2]^+$, cis-$[Cr(bpy)_2(H_2O)_2]^{3+}$, $[Cr(bpy)_2gly]^{2+}$and $[Cr(phen)_2ox]^+$in presence of (+)-cinchonine HCl, (-)-cinchonidine HCl and (+)-trataric acid were measured between 700-400 nm. The band positions alongwith their molar ellipticity values are reported in Table VIII,and CD spectra of these systems are reproduced in figures 1-4.

CD spectra of these systems consist of two Cotton effect bands of opposite sign. The CD spectra of cis-$[Cr(phen)_2Cl_2]^+$, cis-$[Cr(bpy)_2Cl_2]^+$, cis-$[Cr(bpy)_2(H_2O)_2]^{3+}$, $[Cr(bpy)_2gly]^{2+}$ in presence of (+)-cinchonine HCl have a negative band (band-I)

Table-VII Physical Data, Metal Analysis and Absorption Spectra of Mixed Ligant Complexes of Chromium(III).

Complex	Colour	Decomp. Temp. °C	Percentage of Cr		Absorption Spectra(cm^{-1}) (ε $M^{-1}cm^{-1}$)
			Calcd.	Found	
$[Cr(phen)_2Cl_2]Cl.3H_2O$	Orange Red	145	9.08	8.8	19,029(77)
$[Cr(bpy)_2Cl_2]Cl.2H_2O$	Bright Red	200	10.25	10.01	19,146(42)
$[Cr(bpy)_2(H_2O)_2]Cl_3$	Greyish Red	170	10.08	10.2	18,867(64)
$[Cr(bpy)_2gly]Cl_2$	Bright Red	180	10.21	9.8	19,230(112)
$[Cr(phen)_2ox]Cl.4H_2O$	Orange Red	230	8.55	8.1	20,202(62)

Table-VIII CD Band Positions and Molar Ellipticity Values of Mixed Ligand Complexes of Cr(III) in Presence of Chiral Environment Substances in Water Solutions.

Complex	Environment Substances	CD Bands			
		Band-I		Band-II	
		ν(cm^{-1})	[θ]	ν(cm^{-1})	[θ]
$[Cr(phen)_2Cl_2]Cl$ (0.025M)	(+)-Cinch.HCl (0.15M)	16,806	-8.0	19,607	+6.0
	(-)-Cinchd.HCl (0.15M)	16,806	+11.9	19,607	-5.0
$[Cr(bpy)_2Cl_2]Cl$ (0.025M)	(+)-Cinch.HCl (0.75M)	16,667	-2.50	19,230	+10.0
	(-)-Cinchd.HCl (0.75M)	16,667	+2.50	19,230	-10.0
	(+)-T.A. (0.1M)	16,667	-0.50	19,230	+7.0
$[Cr(bpy)_2(H_2O)_2]Cl_3$ (0.04M)	(+)-Cinch.HCl (0.12M)	16,949	-6.25	19,607	+8.2
	(-)-Cinchd.HCl (0.12M)	16,949	+6.25	19,607	-7.0
$[Cr(bpy)_2gly]Cl_2$ (0.025M)	(+)-Cinch.HCl (0.20M)	16,667	-2.00	19,230	+5.0
	(-)-Cinchd.HCl (0.20M)	16,667	+2.00	19,230	-5.0
	(+)-T.A. (0.20M)	16,667	-0.50	20,000	+5.0
$[Cr(phen)_2ox]Cl$ (0.025M)	(+)-Cinch.HCl (0.08M)	------	-----	20,000	-1.2
	(-)-Cinchd.HCl (0.08M)	------	-----	20,000	+1.6

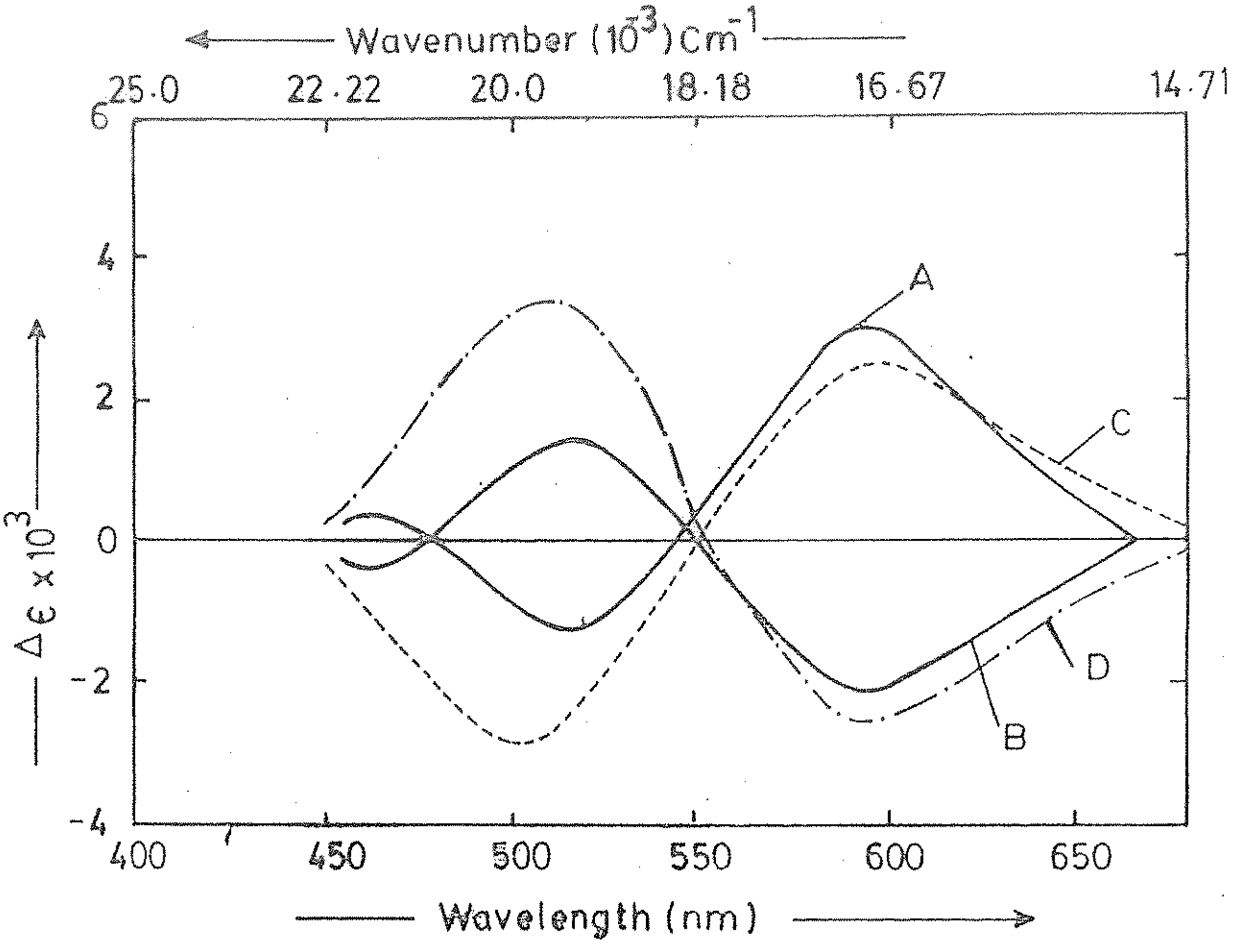


Fig. 1. (A,B) CD Spectra of $[Cr(phen)_2Cl_2]^+$ and $[Cr(bpy)_2(H_2O)_2]^{3+}$ (C,D) in presence of Chiral Environment Substances in Aqueous Solution.

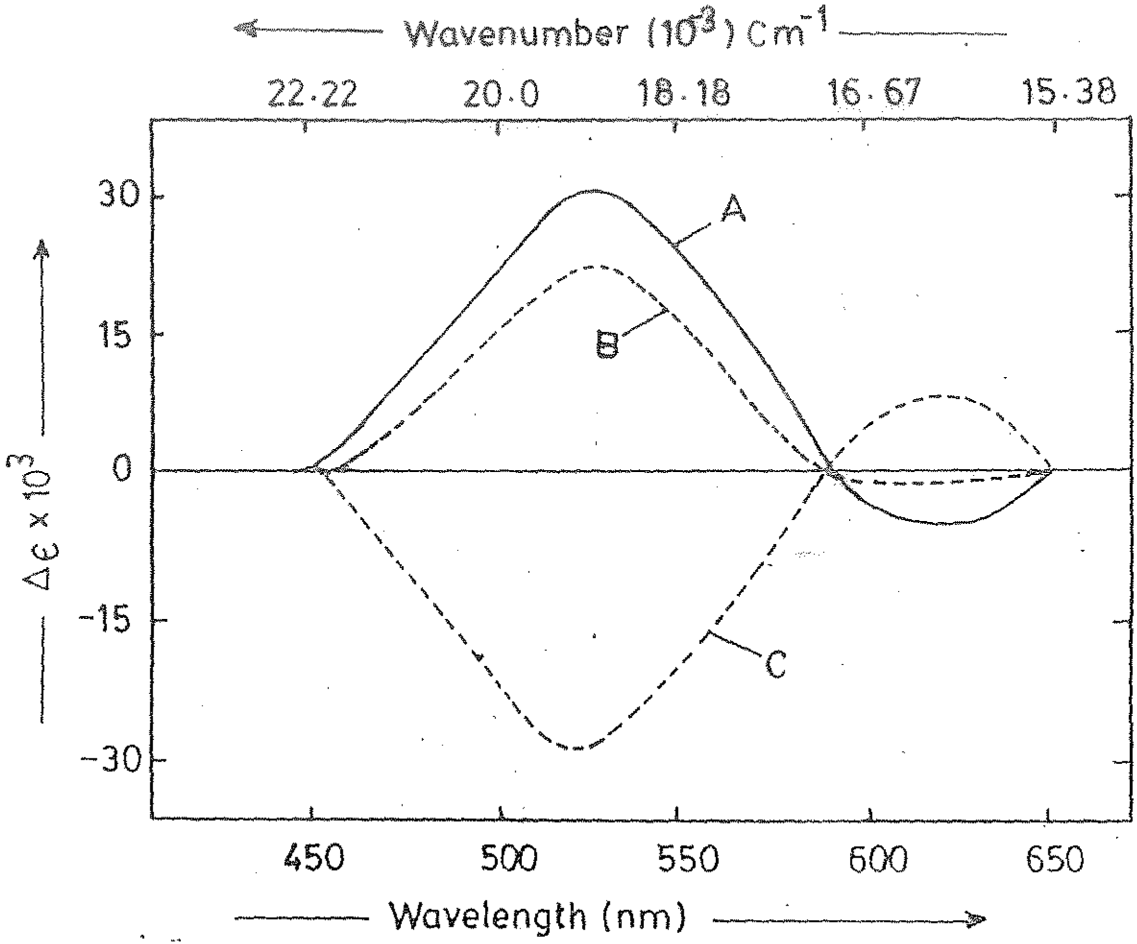


Fig. 2. CD Spectra of $[Cr(bpy)_2Cl_2]^+$ in presence of Chiral Environment Substances in Aqueous Solution.

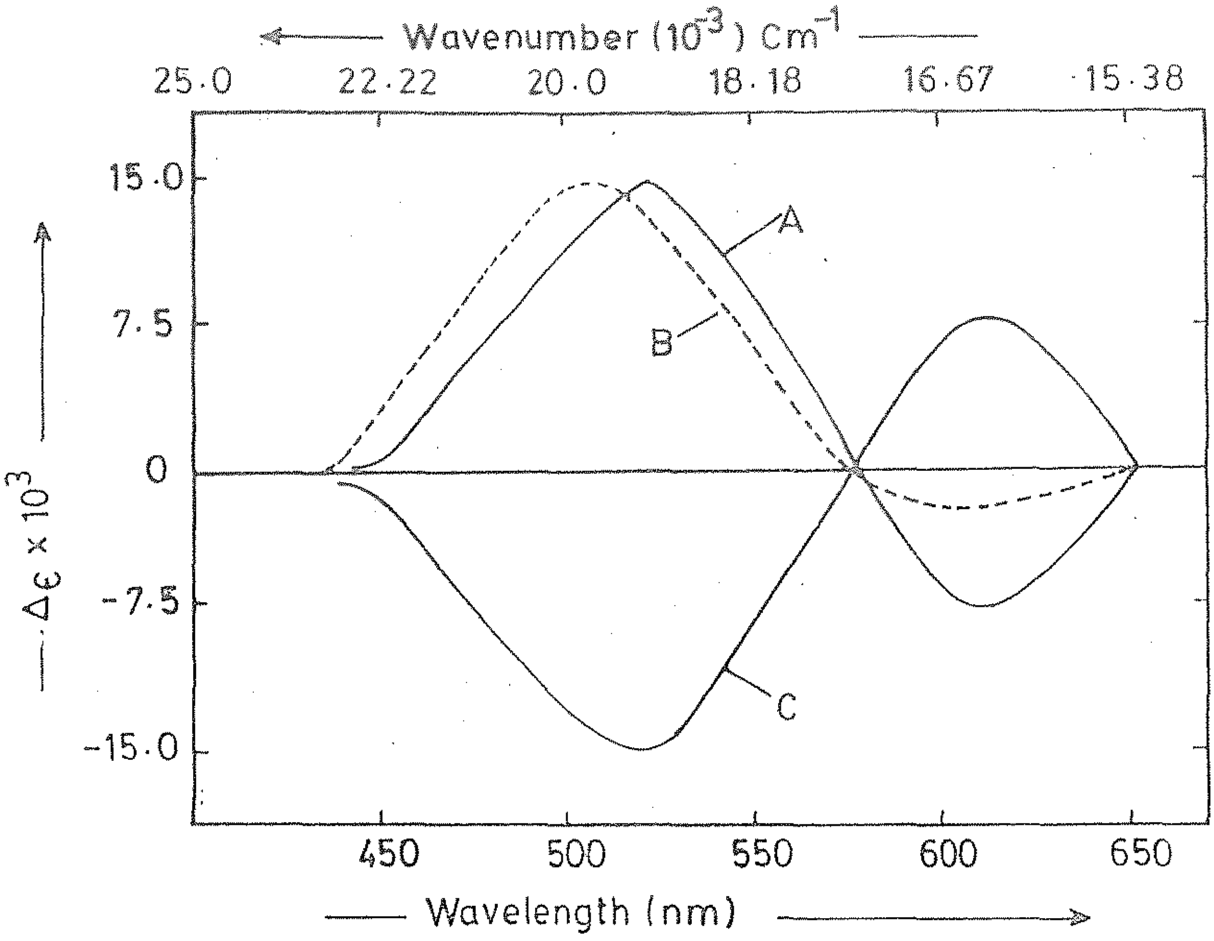


Fig. 3. CD Spectra of $[Cr(bpy)_2gly]^{2+}$ in presence of Chiral Environment Substances in Aqueous Solution.

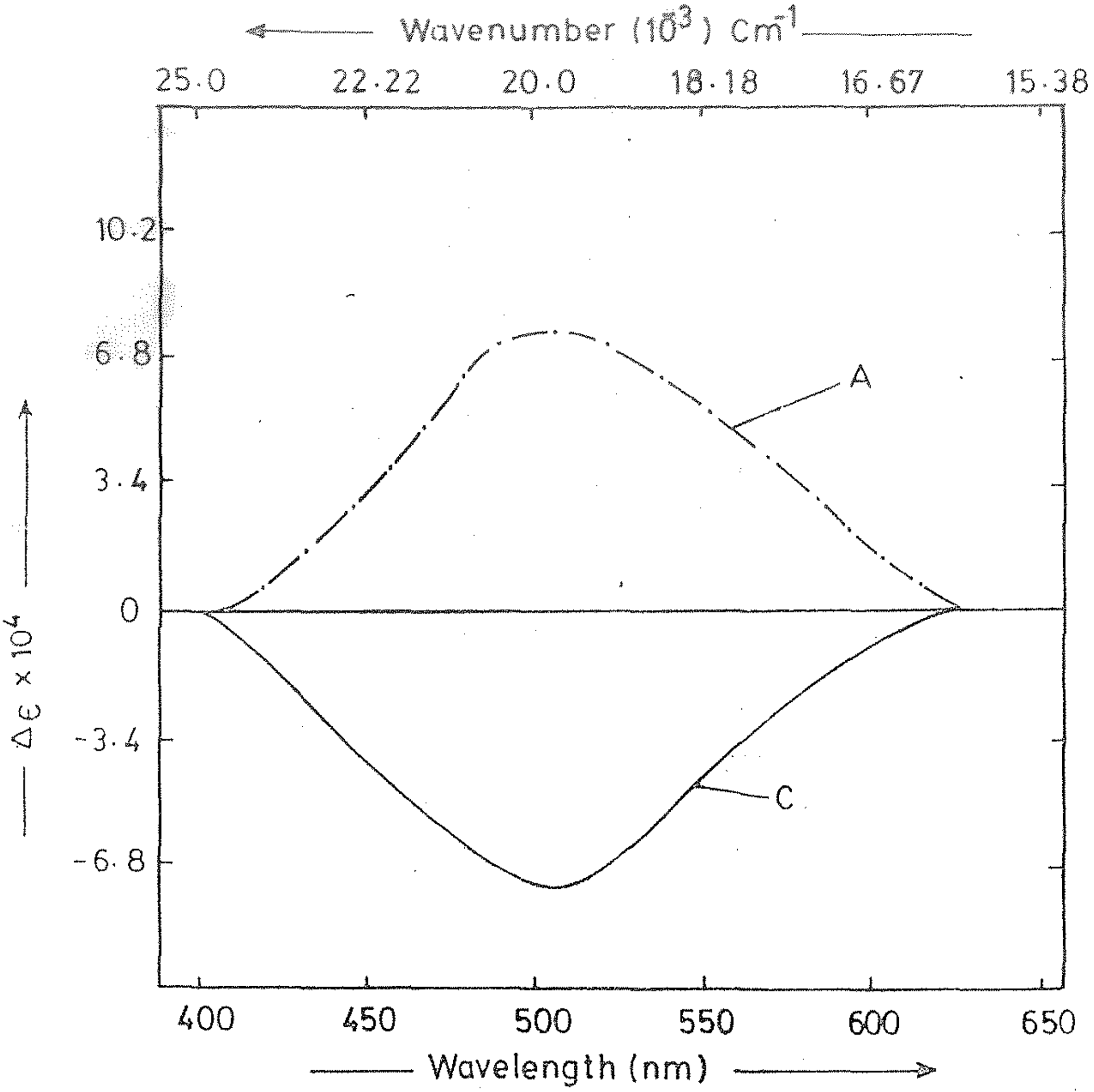
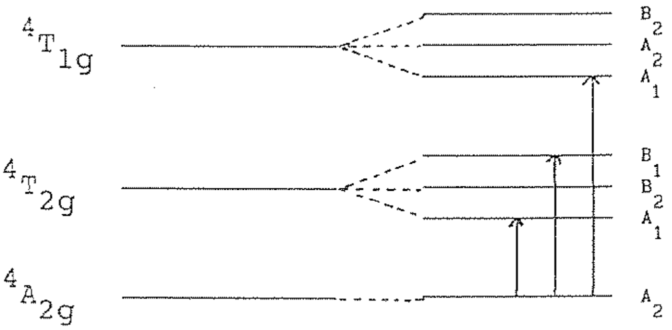


Fig. 4. CD Spectra of $[Cr(phen)_2ox]^+$ in presence of Chiral Environment Substances in Aqueous Solution.

between 16,666 cm^{-1}-16,949 cm^{-1} with molar ellipticity 0.50-11.9 deg l $mole^{-1}cm^{-1}$ and a higher energy positive band (band II) between 19,607-20,000 cm^{-1} with molar elipticity 1.25-10 deg l $mole^{-1}cm^{-1}$. The CD of these complexes in presence of (-)-cinchonidine HCl has a mirror image relationship with those obtained in presence of (+)-cinchonine HCl. All these complexes show a negative Pfeiffer effect in presence of both (+)-cinchonine HCl and (-)-cinchonidine HCl. Therefore it may be assumed that CD spectra of these complexes in presence of (+)-cinchnine HCl are due to *levo* enantiomer, while those obtained in presence of (-)-cinchonidine HCl arise from the dextro rotatery enantiomer two complexes $[Cr(bipy)_2Cl_2]^+$ and $[Cr(bipy)_2gly]^{2+}$ also showed CD bands in presence of (+)-tartaric acid. The CD spectra of these complexes in presence of (+)-tartaric acid is similar to those obtained in presence of (-)-chinchonidine HCl. The CD spectrum of $[Cr(phen)_2ox]^+$ion in presence of (+)-cinchonine HCl consists of a single negative band centred at 20,000 cm^{-1} while that obtained in presence of (-)-cinchonidine HCl and (+)-tartaric acid consist of a positive band at the same position. The two spectra are mirror image of each other.

Chromium (III) is a d^3 system and has a nondegenerate quartet A_{2g}as ground state in a perfectly octahedral environment. There are three other states $^4T_{2g}$, $^4T_{1g}(F)$ and $^4T_{1g}(P)$ of the same spin multiplicity to which electronic excitations may accur. The absorption spectra of a number of complexes of Cr(III) have been reported, and bands between υ_1 15770-17700 cm^{-1} ($^4A_{2g} \longrightarrow {}^4T_{2g}$), between υ_2 20840-25000 cm^{-1} ($^4A_{2g} \longrightarrow {}^4T_{1g}$) and υ_3 between 32,400-37700 cm^{-1} ($^4A_{2g} \longrightarrow {}^4T_{1g}(P)$] have been assigned. If symmetry of the comlex is reduced, these degenerate excited states will further split and larger number of bands are expected in the absorption spectra. However instead of split bands, considerable broadening of bands is observed in lower symmetry complexes.

All of the above mentioned complexes are dissymmetric and belong to C_2 or C_1 symmetry. The triply degenerate excited states in these complexes should further split to give A_1, A_2 and B_2 states. Excitation of electrons to these non-degenarate levels give rise to larger number of bands. The absorption spectra of these complexes consist of only one broad band between 18,867-20,202 cm^{-1} which seems to arise from excitation of electrons to T_{2g} upper level (υ_1) in octahedral symmetry. Obviously excitation of electrons to non-degenarate upper states has not resulted in seperate bands but only broadening has occured.



CD being very sensetive technique should give seperate bands due to excitation of electrons to non-degenrate levels. Since A_2 is the ground state in these systems, excitation of electrons to A_1 and B_2 non-degenerate levels are dichroic while transition to A_2 will be forbidden and should not be observed.

The couplet of CD bands observed inthese systems are very close and cannot be assigned to either of the two spin allowed transitionsi.e; υ_1 or υ_2 of octahedral field. It seems that these two Cotton bands belong to the same electronic transition i.e; $\upsilon_1(^4A_{2g} \longrightarrow {}^4T_{2g})$ of an octahedral system, arising from excitation of electrons to split levels of T_{2g} state of octahedral symmetry. Therefore band I may arise from excitation of electrons to A_1 upper state while band II may be assigned to transition to B_1 upper state. The only CD band observed for $[Cr(phen)_2ox]^+$ may be assigned to $A_2 \longrightarrow B_2$ transition, while weaker band (band I) observed in other complexes of this series is not observed in this complex.

Absolute Configuration:

The absolute configuration of ligands around the metal ion in these complexes may be correlated with standard complexes on the basis of their Pfeiffer rotation and CD spectra. The complexes (-)-cis-$[Cr(phen)_2Cl_2]Cl$, (-)-cis-$[(Cr(bpy)_2$-$Cl_2]Cl$, (-)-cis-$[Cr(bpy)_2(H_2O)_2]Cl_3$ and (-)-$[Cr(bpy)_2gly]Cl_2$ should have the same absolute configuration around the metal ion as that of (+)-$K_3[Cr(ox)_3]$ or (-)-$K_3[Co(ox)_3$ since all of these enantiomers are enriched in presence of (+)-cinchonine HCl. The complexes (+)$K_3[Cr(ox)_3]$, (-)-$K_3[Co(ox)_3]$ and (+)-$[Co(en)_3]Cl_3$ have been assigned Δ configuration around the metal ion therefore *leva* enantiomers of cis-$[Cr(phen)_2Cl_2]Cl$, cis-$[Cr(bpy)_2Cl_2]Cl$, cis-$[Cr(bpy)_2(H_2O)_2]Cl_3$ and $[Cr(bpy)_2$-gly$]Cl_2$ may be assigned Δ absolute configuration around the metal ion. The *leva* rotarory enantiomer of $[Cr(phen)_2ox]^+$ion was enriched in presence of (+)-cinchonine HCl and shows a negative CD band at 20,000 cm-1 which is opposite in sign to those in other complexes of the series. Therefore (-)-$[Cr(phen)_2ox]^+$ must have an opposite absolute configuration i.e. Λ of ligands around the metal ion.

(b) Pfeiffer CD of $[Cr(malon)_3]^{3-}$:

Pfeiffer CD of $[Cr(malon)_3]^{3-}$ in presence of (-)-cinchonidineHCl, (+)-α-methylbenzylamine HCl, (-)-quinine HCl, (-)-brucine HCl and (-)-ephedrine HCl were measured in aqueous solution. The CD band position alongwith their molar ellipticity values of this complex ion are given in Table-IX The CD spectra in presence of various environment substances are reproduced in figure 5. The Pfeiffer CD of the complex ion in presence of (+)-α-methylbenzylamine HCl and (-)-quinine HCl are representative of *dextra* enantiomers, while those in presence of (-)-cinchonidine HCl, (-)-brucine HCl and (-)-ephedrine HCl

Table-IX CD Spectral Data of $K_3[Cr(malon)_3]$ in Presence of Various Environment Substances in Aqueous Solution.

Complex	Environment Substances	CD Bands			
		Band-I		Band-II	
		$\nu(cm^{-1})$	$[\theta]$	$\nu(cm^{-1})$	$[\theta]$
$K_3[Cr(malon)_3]$ (0.03M)	(+)-α-MBA.HCl (0.12M)	17,543	+19.8	23,255	-3.3
	(-)-Cinchd.HCl (0.12M)	17,543	-19.8	23,255	+3.3
	(-)-Quinine.HCl (0.12M)	18,181	+13.2	24,390	-10.0
	(-)-Ephed.HCl (0.12M)	17,543	-19.8	23,255	+3.3
	(-)-Bruc.HCl	17,543	-7.5	23,255	+5.0

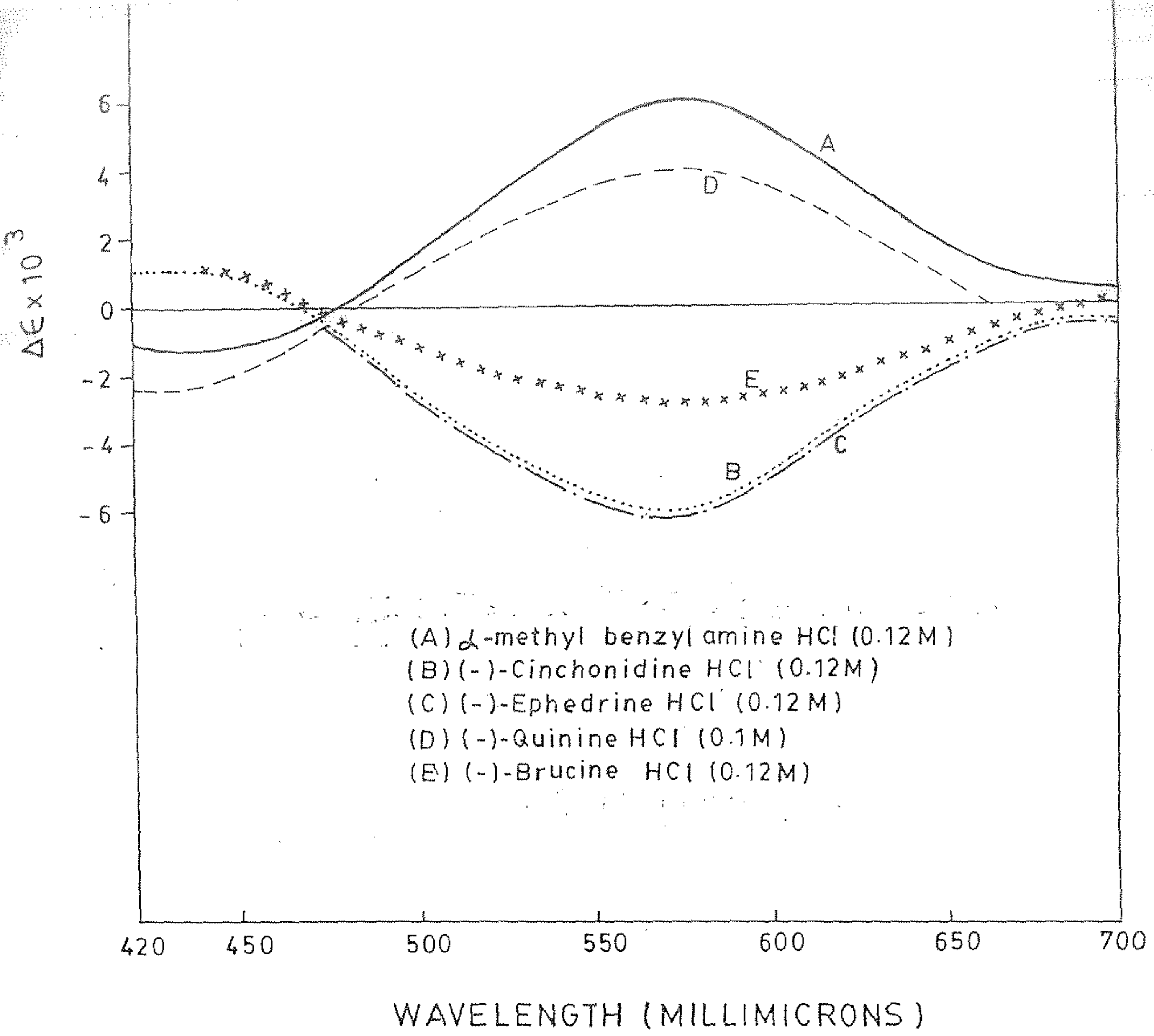


Fig. 5. CD Spectra of $[Cr(malon)_3]^{3-}$ in presence of Chiral Environment Substances in Aqueous Solution.

are representative of *levo* enantiomers. The CD spectra of this complex ion consist of two bands, band I, centred at 17,543-18,181 cm^{-1} with molar ellipticity 13.2-19.8 deg l $mole^{-1}$ cm^{-1} and band II btween 23,255-24,390 cm^{-1} with molar ellipticity 3.3-10 deg l $mole^{-1}$ cm^{-1}. The CD spectra of the *dextro* and *levo* enantiomer are mirror image of each other.

The CD spectrum of (-)-$[Cr(malon)_3]^{3-}$ has already been reported[63]. It consists of two bands of oposite sign centred at 18,018 cm^{-1} and 23,094 cm^{-1}. The position of the observed bands in the Pfeiffer effect system containing racemic $[Cr(malon)_3]^{3-}$ and the environment substances are very close to those already reported. These CD bands have been assigned to various transitions. The band at 18,018 cm^{-1} is assigned to the transition to A_2 state and that observed at 23,094 cm^{-1} is assigned to excitation of electrons to E_b upper level. Therefore band I observed at 17,543 cm^{-1} may be assigned to transition to A_2 level and band II at 23,255 cm^{-1} may be due to transation to E_b level. The small variation in band position of the Pfeiffer systems are mainly due to the instrument. The instrument can only record ellipticity values upto a certain lower limit. The displacement in dl equillibrium in these systems is only 1-2 % resulting in a very small enrichment of one enantiomer. The CD bands are shifted in very dilute solutions, which is observed in these systems. Some sort of association between the chiral environment substance and racemic complexes may also be responsible for slight shifting in Cotton band positions of these complexes.

(c) Pfeiffer CD Spectra of Polyamine Carboxylic Acid Comploxes:

The Pfeiffer effect in metal complexes of sexadentate polyamine carboxylate ions like $EDTA^{4-}$ and $DTPA^{5-}$ have been investigated to a lesser extent. In fact this effect was reported only in $[Cu(EDTA)]^{2-}$ in presence of (-)-quinine HBr in 1956[24]. Complexes of this type i.e; $[M(EDTA)]^{n-}$ are dissymmetric and exist as enantiomeric pair. Only K[Co(EDTA)] has been resolved and its CD spectrum reported by Dwyer et.al.[64]. The analogous chromium(III) complex formulated as $[Cr(EDTA)H_2O]^-$have never been resolved, which is surprising since chromium (III) complexes have comparable inertness and stability to those of Cobalt(III). Similarly $[Cr(DTPA)]^{2-}$is a stable six coordinated complex and should be dissymmetric.

The complexes $Na[Cr(EDTA)H_2O]$ and $Na_2[Cr(DTPA)]$ are dark purple crystalline compounds which dissolve in water to give dark purple solution. The absorption spectra of aqueous solutions of these two complexes consist of bands between 17,699-18,181 $cm^{-1}$and 21975-25,000 cm^{-1} with extinction coefficients between 200-225 M^{-1} cm^{-1}. These two bands may be assigned to υ_1 and υ_2 spin allowed transitions to triply degenerate upper states in actahedral field. A number of workers have studied absorption spectra of Chromium (III) complexes and assigned bands between 17,400 — 21,850 cm^{-1} to υ_1 and 24,600 — 28,450 cm^{-1} υ_2 transitions.[65]

These two complexes show positive Pfeiffer effect in presence of (-)-cinchonidine HCl, (+)-α-methylbenzylamine HCl (+) and (-)-tartaric acids while a negative Pfeiffer effect was observed in presence of (+)-ascorbic acid. The rotational changes are very small mainly due to low concentration of the complexes used. The CD spectrum of $[Cr(EDTA)H_2O]^-$ was recorded in presence of (+)-cinchonine HCl, (-)-cinchonidine HCl, (+)-ascorbic acid, (+)-tartaric acid and (-)-tartaric acid. Due to high colour intensity of the complexes concentrations of the complexes and environment substances were maintained at 0.025M and 0.1M respectively. The *dextra* enantiomers of $[Cr(EDTA)H_2O]^-$ ion is enriched in presence of (+)-cinchonine HCl and (+)-tartaric acid while (-)-cinchonidine HCl, (-)-tartaric acid and (+)-ascorbic acid enriched the *leva* enantiomers. CD spectra of this complex is represented in Figure 6 and CD data is given in table -X. The CD spectrum of $[Cr(EDTA)H_2O]^-$ in presence of (+)-cinchonine HCl consists of two bands of opposite sign a positive band (band I) at 17,857 cm^{-1} and a relatively weaker negative band (band II) at 20,408 cm-1. In presence of (-)-cinchonidine HCl a mirror image spectrum was obtained. The CD spectrum of this ion in presence of (+) and (-)-tartaric acid and (+) ascorbic acid consists of a broader CD band centered at 17857 cm^{-1}, while the weaker CD band was lost in the noise of

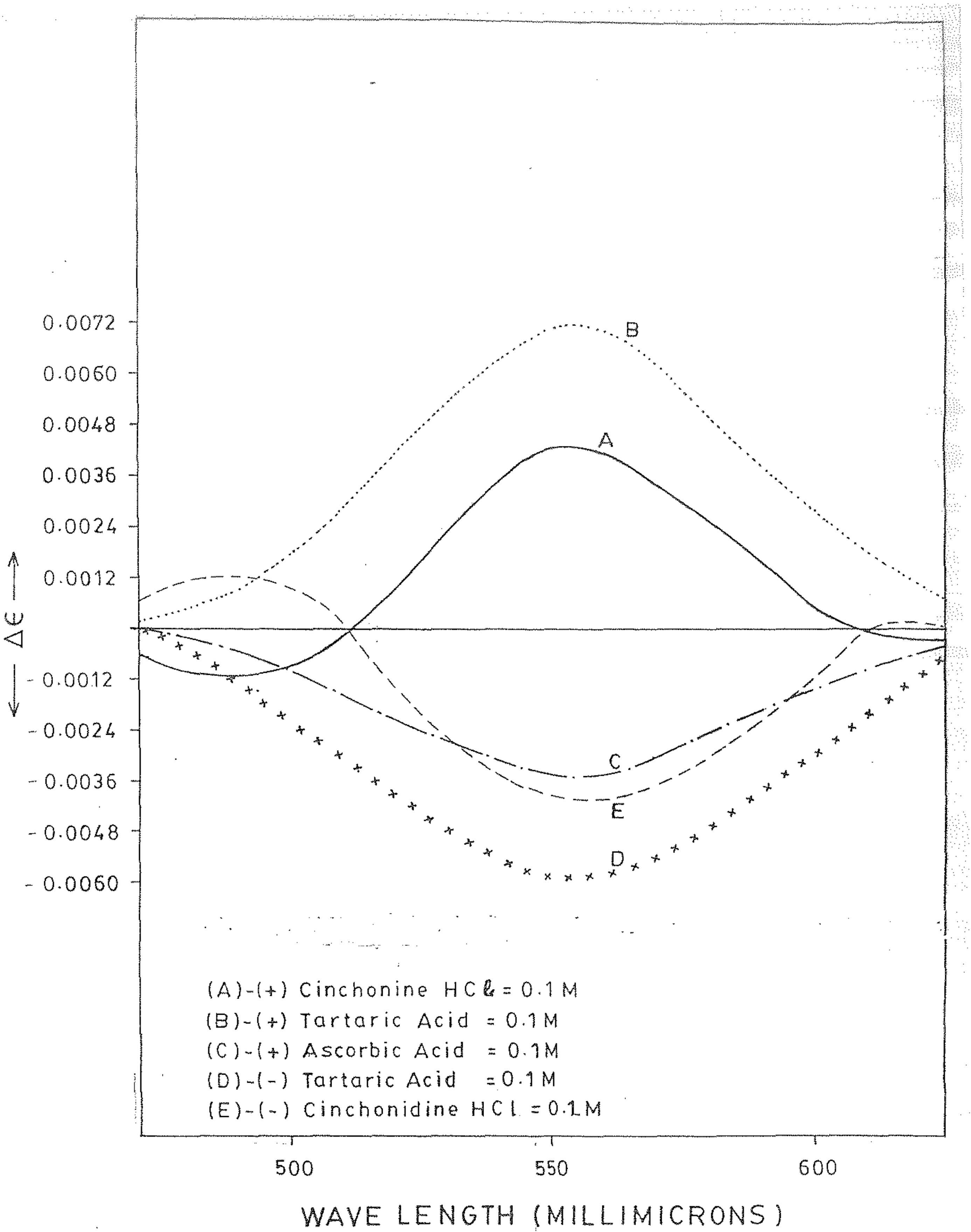


Fig: 6. CD Spectra of $[Cr(EDTA)H_2O]^-$ in presence of Chiral Environment Substances in Aqueous Solution.

0.015M

Table- X CD Spectral Data of $EDTA^{4-}$ and $DTPA^{5-}$ Complexes of Cr(III) in Presence of Chiral Environment Substances in Aqueous Solution.

Complex	Environment Substances	CD Bands			
		Band-I		Band-II	
		ν(cm^{-1})	[θ]	ν(cm^{-1})	[θ]
Na[Cr(EDTA)H_2O]	(+)-Cinch.HCl	17,857	+14.0	20,408	-4.0
(0.025M)	(0.1M)				
	(-)-Cinchd.HCl	17,857	-14.0	20,408	+4.0
	(0.1M)				
	(+)-T.A.	17,857	+12.0	------	----
	(0.1M)				
	(-)-T.A.	17,857	-12.0	------	----
	(0.1M)				
	(+)-A.A.	17,857	-20.0	------	----
	(0.1M)				
Na_2[Cr(DTPA)]	(+)-T.A.	19,230	+16.0	23,809	-1.65
(0.03M)	(0.12M)				
	(+)-α-MBA.HCL	19,230	+9.9	23,809	-1.65
	(0.12M)				
	(+)-A.A.	19,230	-11.5	23,809	+3.3

the instrument.

The CD spectrum of $[Cr(DTPA)]^{2-}$ in presence of L(+)-tartaric acid and (+)-α-methylbenzylamine HCL is representative of *dextra* enantiomer, while that obtained in presence of (+)-ascorbic acid is due to *leva* enantiomer. CD spectra are reproduced in Figure 7 and CD spectral data is given in table-X. A stronger positive band centerd at 19,230 cm^{-1} and a weaker negative band centred at 23,809 cm^{-1}were observed in presence of (+)-tartaric acid and (+)-α-methylbenzylamine HCl while a mirror image spectrum was obtained in presence of (+)-ascorbic acid. A comparison of absorption and CD spectra of these two complex ions revealed that couplet of bands in CD are closer to the lower energy absorption band assigned to υ_1 in these systems while the second spin allowed treansition υ_2 is observed at a much higher energy. The couplet of CD bands seem to arise from excitation of electrons to undimensional components of $^4T_{2g}$ upper state. Therefore band I may be assigned to transition $^4A_2 \longrightarrow {}^4A_1$ and $^4A_2 \longrightarrow {}^4B_2$ while $^4A_2 \longrightarrow {}^4A_2$ is not observed because it is forbidden by selection rules.

Absolute Configuration:

The absolute configuration of complex ions $[Cr(malon)_3]^{3-}$, $[Cr(EDTA)H_2O]^-$ and $[Cr(DTPA)]^{2-}$ may be assigned by comparing their signs of Pfeiffer effect and CD bands to those of the standard complexes. Since $(+)-[Cr(malon)_3]^{3-}$ and

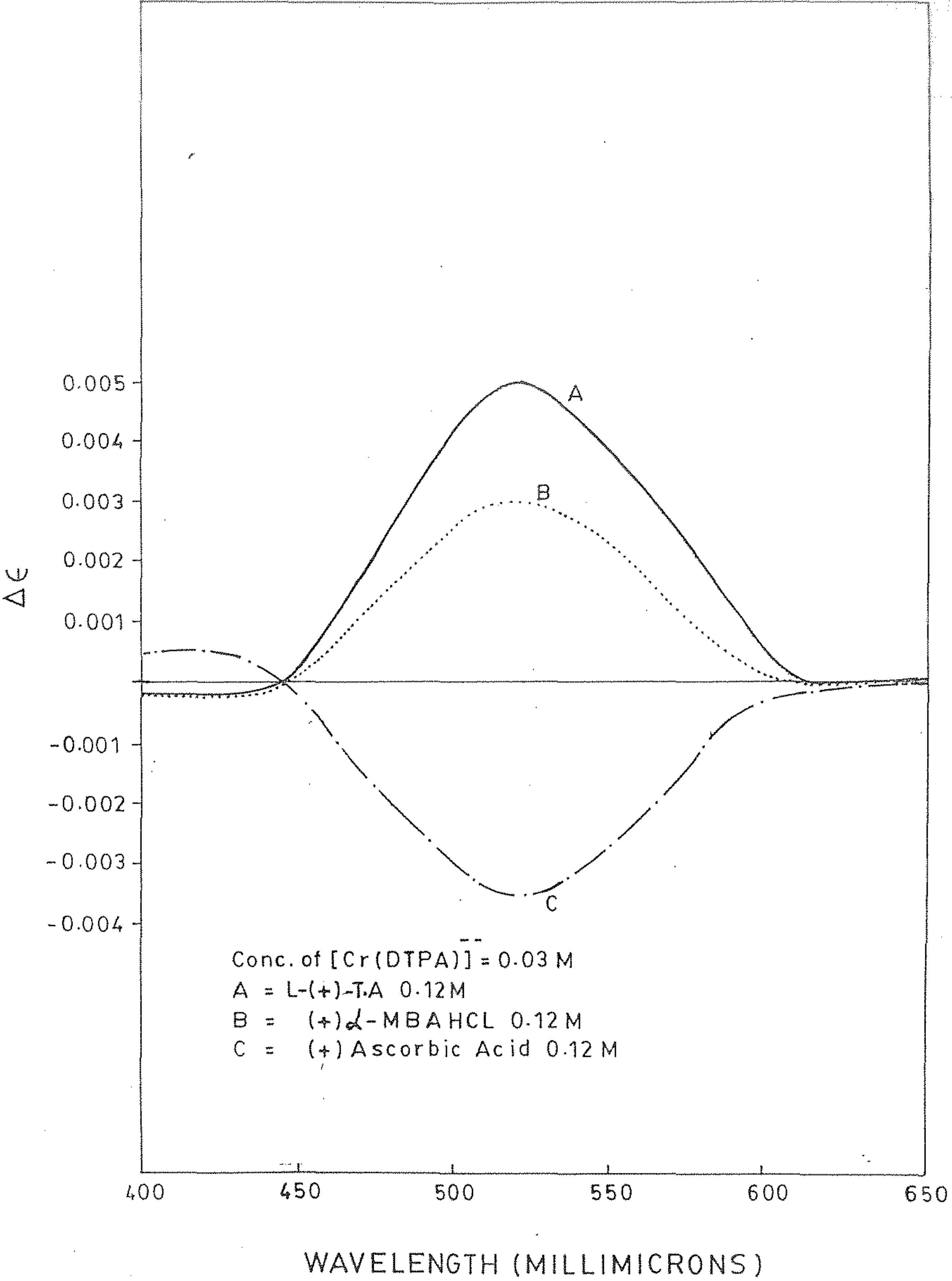


Fig: 7. CD Spectra of $[Cr(DTPA)]^{2-}$ in presence of Chiral Environment Substances in Aqueous Solution.

$(+)$-$[Cr(EDTA)H_2O]^-$ are enriched in presence of $(+)$-cinchonine HCl and have similar CD spectra, therefore they should have the same absolute configuration. These two complex ions may be assigned a Δ absolute configuration. Further $(+)$-$[Cr(EDTA)H_2O]^-$ and $(+)$-$[Cr(DTPA)]^{2-}$ ions are enriched in presence of $(+)$-tartaric acid. They have also similar CD spectral bands in presence of this environment compound. Therefore these complexes may be assigned Δ absolute configuration around the metal ion.

It may be concluded that *dextra* enantiomers of $[Cr(malon)3]^{3-}$, $[Cr(EDTA)H_2O]^-$ and $[Cr(DTPA)]^{2-}$ all have the same Δ absolute configuration, while their *leva* enantiomers may be assigned a Λ absolute configuration arround the metal ion.

(d) Pfeiffer CD of $[V(EDTA)]^-$ and $[V(DTPA)]^{2-}$:

The CD spectrum of $[V(EDTA)]^-$ ion in presence of $(-)$-cinchonidine HCl, $(+)$-α-methylbenzylamine HCl, $(-)$-brucine HCl and $(-)$-tartaric acid are similar and arise from the *dextra* enantiomer, while that obtained in presence of $(+)$-tartaric acid and $(-)$-ephedrine HCl are similar and representative of *leva* enantiomer. The CD spectrum of this ion in presence of former group ~~of~~ environment substances is a mirror image of that obtained in presence of the later two environments. At low concentration of the complex ion (0.035M) and environment substances (0.1M) a broad, weak CD band was observed. However two well defined CD bands appeared in presence of 3-4 fold higher concentrations of both the complex and the environment compounds. The band positions and molar ellipticity values are given in table-XI . CD spectra of these Pfeiffer systems are reproduced in Fig 8.

The CD spectrum of $[V(EDTA)]^-$ complex ion in presence of (-)-cinchonidine HCl, (+)-α-methylbenzylamine HCl, (-)- brucine HCl and (+)-tartaric acid consists of a positive Cotton band I at 19,607 cm^{-1} with molar ellipticity values 2-8 deg l $mole^{-1}cm^{-1}$ and a negative weaker band II at 23,255cm^{-1} with molar ellipticity values between 1-2 deg l $mole^{-1}cm^{-1}$. In order to explore any interaction between V^{3+} ion and the chiral environment compounds, CD spectra of aqueous solutions containing Vanadium(III) chloride and chiral environents (1:3 mole ratio) were studied. These spectra had no bands in the visible region (400-650nm) where crystal field bands are commonly expected, thus ruling out any interaction between the chiral environment substances and the metal ion. However CD spectrum of aqueous VCl_3 in presence of (+)-tartaric acid has two bands at 18,350cm^{-1} and 29,411cm^{-1}, which are similar to those already reported for VO-(+)-tartrate system[66]. It seems that V^{3+} ion is instantaneously oxidized to oxovanadium (IV) ion in presence of (+)-tartaric acid.

It was observed during this study that colour of the solution containing $[V(EDTA)]^-$ and (-)-cinchonidine HCl

Table-XI CD Spectral Data of Na[V(EDTA)] and $Na_2[V(DTPA)]$ in Presence of Various Environment Substances in Aqueous Solution.

Complex	Environment Substances	CD Bands			
		Band-I		Band-II	
		$\nu(cm^{-1})$	$[\theta]$	$\nu(cm^{-1})$	$[\theta]$
Na[V(EDTA)] (0.1M)	(+)-α-MBA.HCl (0.3M)	19,607	+6.4	23,255	-2.0
	(-)-Cinchd.HCl (0.3M)	19,607	+8.4	23,255	-1.0
	(-)-Ephed.HCl (0.12M)	19,607	-4.8	23,255	+1.2
	(+)-T.A. (0.3M)	19,607	+2.4	23,255	-1.0
	(-)-Brucn.HCl (0.12M)	19,607	+4.4	23,255	-1.5
$Na_2[V(DTPA)]$ (0.1M)	(-)-Cinchd.HCl (0.3M)	16,229	-2.2	21,276	+9.0
	(+)-α-MBA.HCl (0.3M)	16,229	-1.2	21,276	+5.0

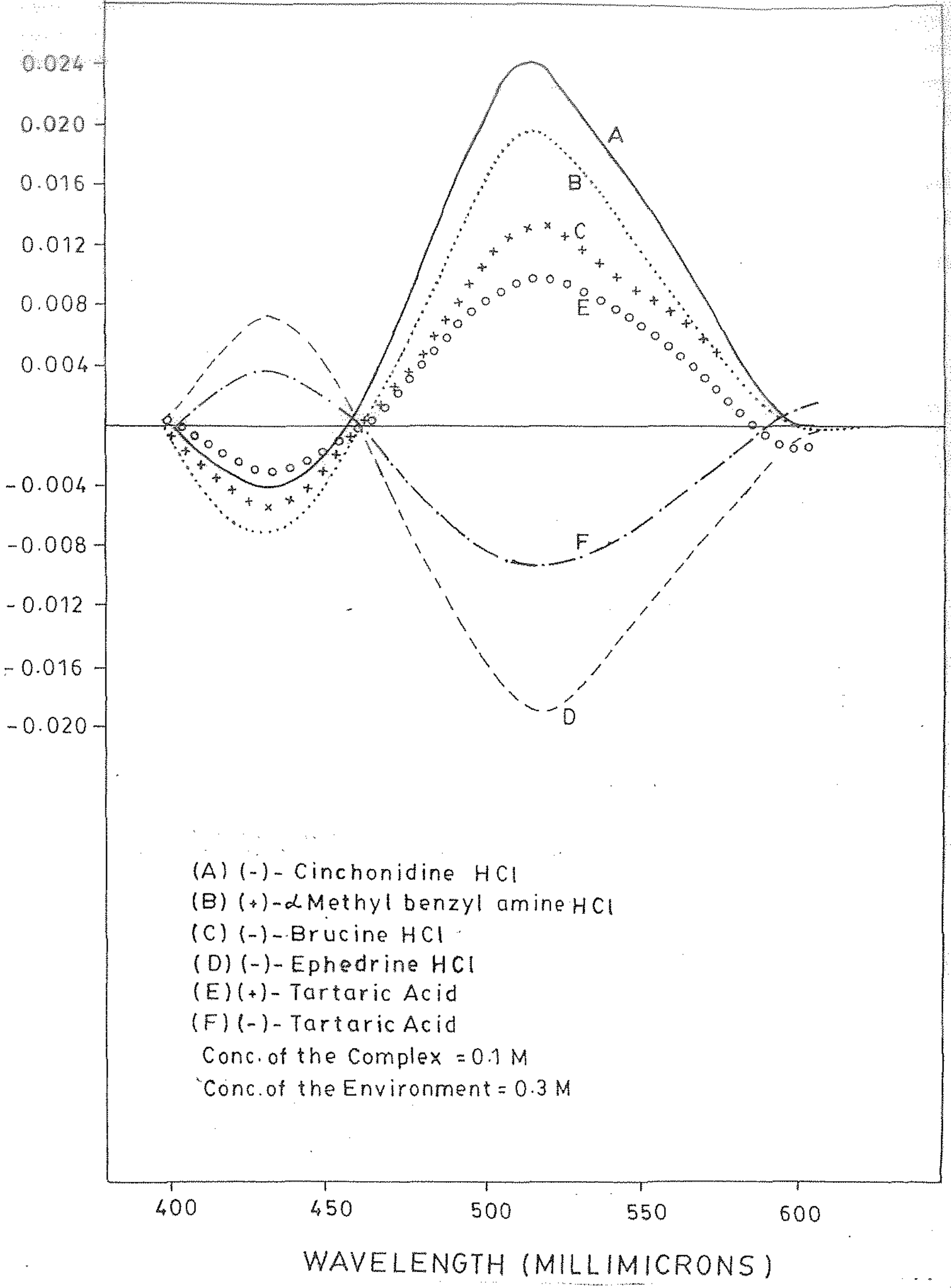


Fig: 8. CD Spectra of $[V(EDTA)]^-$ in presence of Chiral Environment Substances in Aqueous Solution.

gradually changed. After about two weaks time, the dark brown colour of $[V(EDTA)]^{-}$ ion was completely changed to blue. The CD spectrum of this blue solution (as reported in Fig 9), consists of a negative band at 17857 cm^{-1} and there is indication of a positive band in lower frequency region.

The complex $[VO(EDTA)]^{2-}$ was prepared by mixing equimolar quantities of $VO(CH_3COO)_2$ and Na_2 EDTA in aqueous solution. The CD spectrum of a solution containing $[VO(EDTA)]^{2-}$ and (-)-cinchonidine HCl (0.1M and 0.3M respectively) was recorded and compared with that obtained for a two weeks old solution containing $[V(EDTA)]^{-}$ and (-)-cinchonidine HCl (0.1M 0.3M). These two CD sepectra match in all details, thus confirming that oxidation of V^{3+} ion into VO^{2+} in pre~~e~~sence of (-)-cinchonidine HCl had occured. The CD spectrum of $[V(EDTA)]^{-}$ in presence of (+)-tartaric acid was essentially similar to that obtained in presence of (-)-cinchonidine HCl. However CD spectrum of this system rapidly changed to that of VO-tartrate ion, indicating that V^{3+} ion was oxidized to VO^{2+} ion in presence of tartrate ion and at the same time (+)-tartrate ion replaced $EDTA^{4-}$ ligand. This is surprising because $EDTA^{4-}$ is a much stronger ligand as compared to (+)-tartrate ion. It seems that the equillibrium,

$$[VO(EDTA)]^{2-} + (+)\text{-tart}^{2-} \rightleftharpoons (VO((+)\text{-tart})] + EDTA^{4-}$$

was shifted towards right hand side, due to higher concen

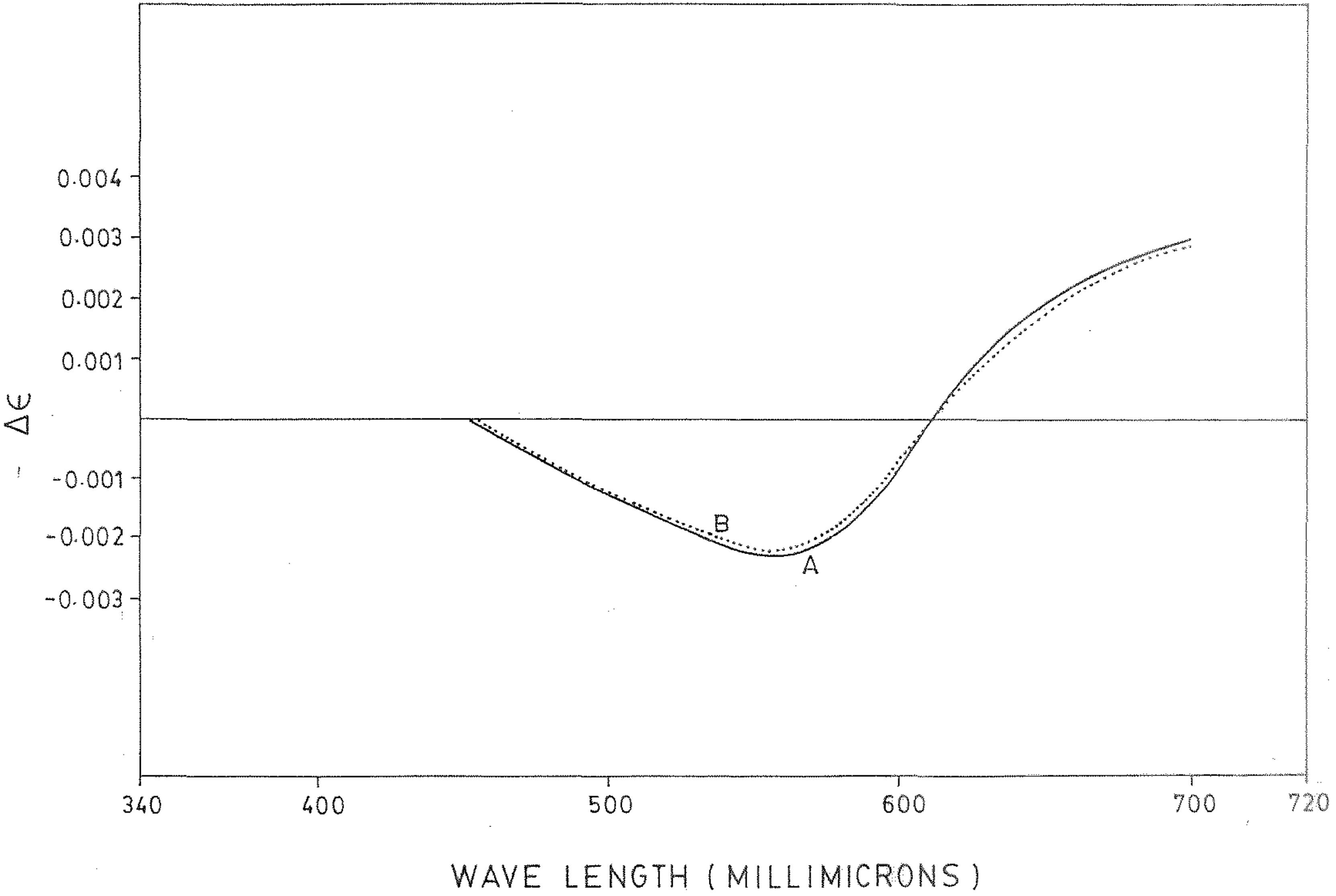


Fig.9. (A) CD Spectrum of $[V(EDTA)]^-$(0.1M) in Presence of (-) Cinchonidine HCl(0.3M) recorded after two w
(B) CD Spectrum of $[VO(EDTA)]^-$ (0.1M) in Presence of (-) Cinchonidine HCl (0.3M).

tration of (+)-tartrate ion in the system.

The CD spectrum of $[V(DTPA)]^{2-}$ ion in presence of (-)-cinchonidine HCl and (+)-α-methylbenzylamine HCl also consists of a couplet of bands, a positive band (band II) at 20,408 cm^{-1} and a weaker negative (band I) at 15,873 cm^{-1}. The CD spectral data is given in table 10 and the CD spectra are reproduced in Fig 10. The CD of $[V(DTPA)]^{2-}$ ion in presence of (+)-tartaric acid was similar to that of VO-(+)tartrate system indicating oxidation of V^{3+}ion and replacement of $DTPA^{5-}$ by tartrate ion in the coordination sphere of the complex ion.

The V^{3+}ion being d^2 system has $^3T_{1g}$ as ground state and $^3T_{2g}$, $^3A_{2g}$and $^3T_{1g}(P)$ as excited states in a perfectly octahedral environment. The crystal field spectra of V(III) complexes is expected to show three bands due to spin allowed transitions to these excited states. The absorption spectra of a number of six coordinated complexes of this ion have been reported which usually consist of two main absorption bands between 12,200-18,640 cm^{-1} and 22,100-28,600 cm^{-1}. 65,67,68 These bands have been assigned to $^3T_{1g} \longrightarrow {}^3T_{2g}(\upsilon_1)$ and $^3T_{2g} \longrightarrow {}^3T_{1g}(P)$ (υ_3) respectively. The excitation of electrons to $^3A_{2g}$ upper level is commonly not observed in octahedral complexes of V^{3+}ion.

The absorption spectrum of $[V(EDTA)]^-$ consists of two bands centred at 12,500 cm^{-1} and 22,600 cm^{-1} which may be assigned to υ_1 and υ_3 respectively. However a shoulder band at

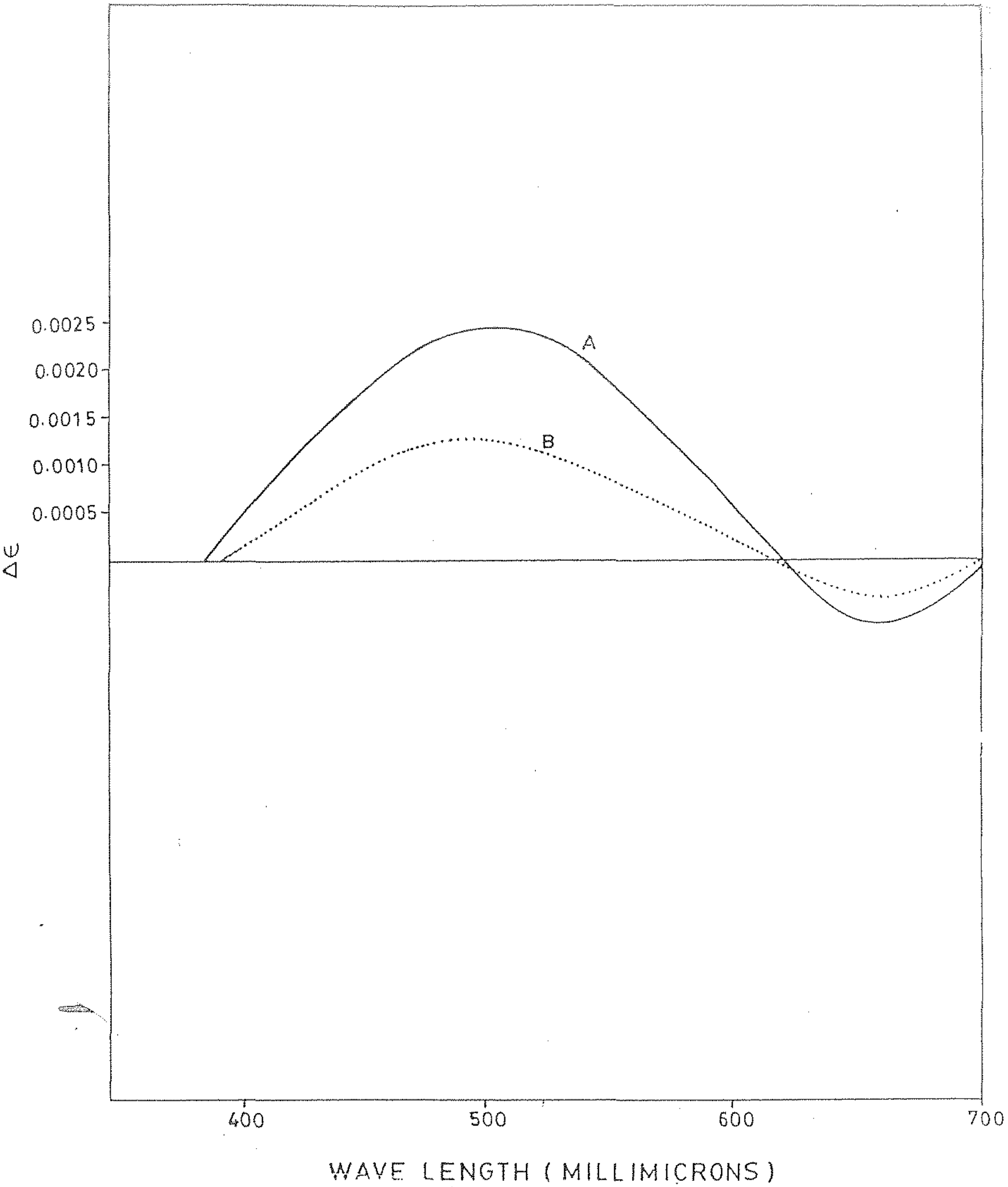
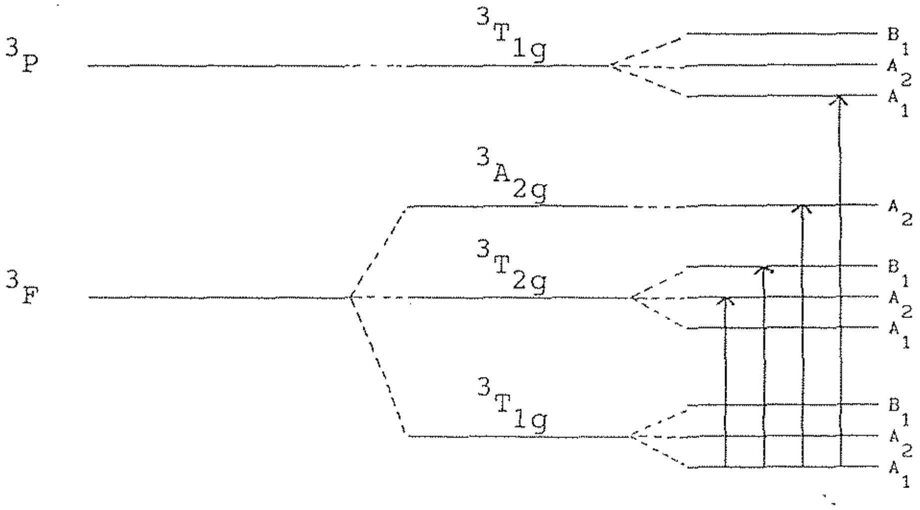


Fig. 10 CD Spectra of $[V(DTPA)]^{2-}$ (0.1 M) in presence of
(A) (−)-Cinchonidine HCl (0.3 M) (B) (+)-α methyle benzyle amine HCl(6·

19,400 cm^{-1} has also been reported for this complex,[69] which may be arising from splitting of triply degenerate $^3T_{1g}(P)$ upper level due to lower symmetry of the complex or due to a spin forbidden transition.

The two Cotton bands in CD spectrum of $[V(EDTA)]^-$ in presence of chiral environment substances are relatively closer and cannot be assigned to υ_1 and υ_3 transitions of octahedral species. These two bands seem to arise from excitation of electrons to nondegenerate components of $^3T_{1g}(P)$ state of octahedral symmetry. In this low symmetry complex ion (C_2) the ground state as well as excited states are nondegenerate and so a larger number of bands are expected. However the major spin allowed bands seem to arise from $A_1 \longrightarrow A_2(^3T_{1g}(P))$ and $A_1 \longrightarrow B_1(^3T_{1g}(P))$ transitions.



The lower energy band I at 19,607cm^{-1}may be assigned transition $A_1 \longrightarrow A_2$ ($^3T_1g(P)$) while higher energy band II may be assigned to $A_1 \longrightarrow B_1$ ($^3T_{1g}(P)$) transition. A number of other possible electronic transitions such as $A_1 \longrightarrow A_1$ ($^3T_{2g}$), $A_1 \longrightarrow A_1$ ($^3T_{1g}(P)$) and $A_1 \longrightarrow A_1$ ($^3A_{2g}$) may not be observed as they are not dichroic. The band II in CD spectrum of $[V(DTPA)]^{2-}$ ion is similar in sign and intensity to band I of $[V(EDTA)]^-$ ion and may be assigned to $A_1 \longrightarrow A_2$ ($^3T_{1g}(P)$) transition. The lower energy band I of this complex ion may be assigned to $A_1 \longrightarrow B_1$ ($^3T_{2g}$) transition.

The absorption spectrum of $[VO(EDTA)]^{2-}$ ion consits of only two bands at 12,800cm^{-1} and 17,200 cm^{-1}. These two bands arise from excitation of electrons to split levels of degenerate states. The V^{4+} being a d^1 system is expected to show only one absorption band in an octahedral field. However due to lower symmetry of the complexes like $[VO(EDTA)]^{2-}$ ion, splitting of higher energy degenerate states occur and two absorption bands are commonly observed. The absorption spectra of six coordinated vanadyl complexes usually consist of three bands as I 10,225-14,400cm^{-1}, II 11,600-18,345 cm^{-1} and III 15,500-21,383 cm^{-1}.[70] These bands have been assigned to excitation of electrons to E, B_1 and A_1 upper states respectively.

The CD spectrum of $[VO(EDTA)]^{2-}$ in presence of (-)-cinchonidine HCl consists of a broad band at 17,857 cm^{-1}, and presence of second positive Cotton band is indicated in lower frequency region. The negative band is comparable to the absorption band at 17,200 cm^{-1} and may be assigned to A ⟶ B transition in a lower symmetry d^1 system.

Absolute Configuration of $[V(EDTA)]^-$ AND $[V(DTPA)]^{2-}$:

The absolute configuration of these complex ions may be assigned by comparing their Pfeiffer effect and CD spectra with those of standard compounds like Δ-$[Co(phen)_3]Cl_2$. The CD spectrum of the Pfeiffer system (+)-$[V(EDTA)]^-$ in presence of (-)-cinchonidine HCl , (+)-α-methylbenzylamine HCl and (-)-brucine HCl is similar and has positive Cotton bands at lower frequency, which may be compared with positive Cotton bands of (+)-$[Co(phen)_3]^{2+}$ in presence of (+)-tartaric acid and (+)-malic acid. The CD bands of (+)-$[V(EDTA)]^-$ have the same sign as those of (+)-$[Co(phen)_3]^{2+}$ ion, so (+)-$[V(EDTA)]^-$ should have the same absolute configuration as that of (+)-$[Co(phen)_3]^{2+}$ion. The absolute configuration of (+)-$[Co(phen)_3]^{2+}$ ion has already been assigned Δ by comparing its CD spectrum with Δ- $[Co(en)_3]Cl_2$.[62]

It is, therefore, proposed that Δ-$[V(EDTA)]^-$ is enriched in presence of (-)-cinchonidine HCl, (+)-α-methylbenzylamine HCl and (-)-brucine HCl or (+)-tartaric acid whereas Λ-$[V(EDTA)]^-$ is enriched by (-)-ephedrine HCl and (-)-tartaric acid as environment substances. Similarly positive Cotton band at 20,408cm^{-1} in $[V(DTPA)^{2-}]$ in presence of (-)-cinchomidine

HCl and (+)-α-methylbenzylamine HCl is comparable with that of Δ-$[Co(phen)_3]^{2+}$ ion and so (+)- $[V(DTPA)]^{2-}$ should have Δ absolute configuration. Therefore it may be assumed that Δ-$[V(DTPA)]^{2-}$ ion is enriched in presence of (-)-cinchonidine HCl and (+)-α-methylbenzylamine HCl.

(e) CD Studies in Complexes $[Nd(EDTA)]^-$ and $[Pr(EDTA)]^-$:

The CD spectra of $[Nd(EDTA)]^-$ $[Nd(DTPA)]^{2-}$, $[Pr(EDTA)]^-$and $[Pr(DTPA)]^{2-}$ ions were studied in presence of (-)-cinchonidine HCl, (+)-tartaric acid, (+)-α-methylbenzylamine HCl and (+)-histidine as chiral environment compounds. $[Pr(EDTA)]^-$ and $[Pr(DTPA)]^{2-}$ did not show CD bands in presence of any of these environment compounds while the anionic $[Pr(EDTA]^-$ in presence of (+)-tartaric acid exhibited a number of Cotton bands which were representative of already reported CD spectrum of $[Pr(+\ -tart)_3]^{3-}$ complexes,[71]indicating that $EDTA^{4-}$ was replaced by (+)-tartrate ion. The anionic complex $[Nd(EDTA)]^-$ ion in presence of (+)-tartaric acid and (-)-cinchonidine HCl exhibited the Pfeiffer effect. At lower concentration of the complex and (+)-tartaric acid (0.05-0.2M). CD bands were not observed in this system however, at higher concentration of the complex and/or environment substance (0.6-2.0 M) a negative sharp Cotton band at 17,182 cm^{-1} was developed. The solution absorption spectrum of this complex ion also cosists of a strong sharp band at this wavelength (Fig.11). The

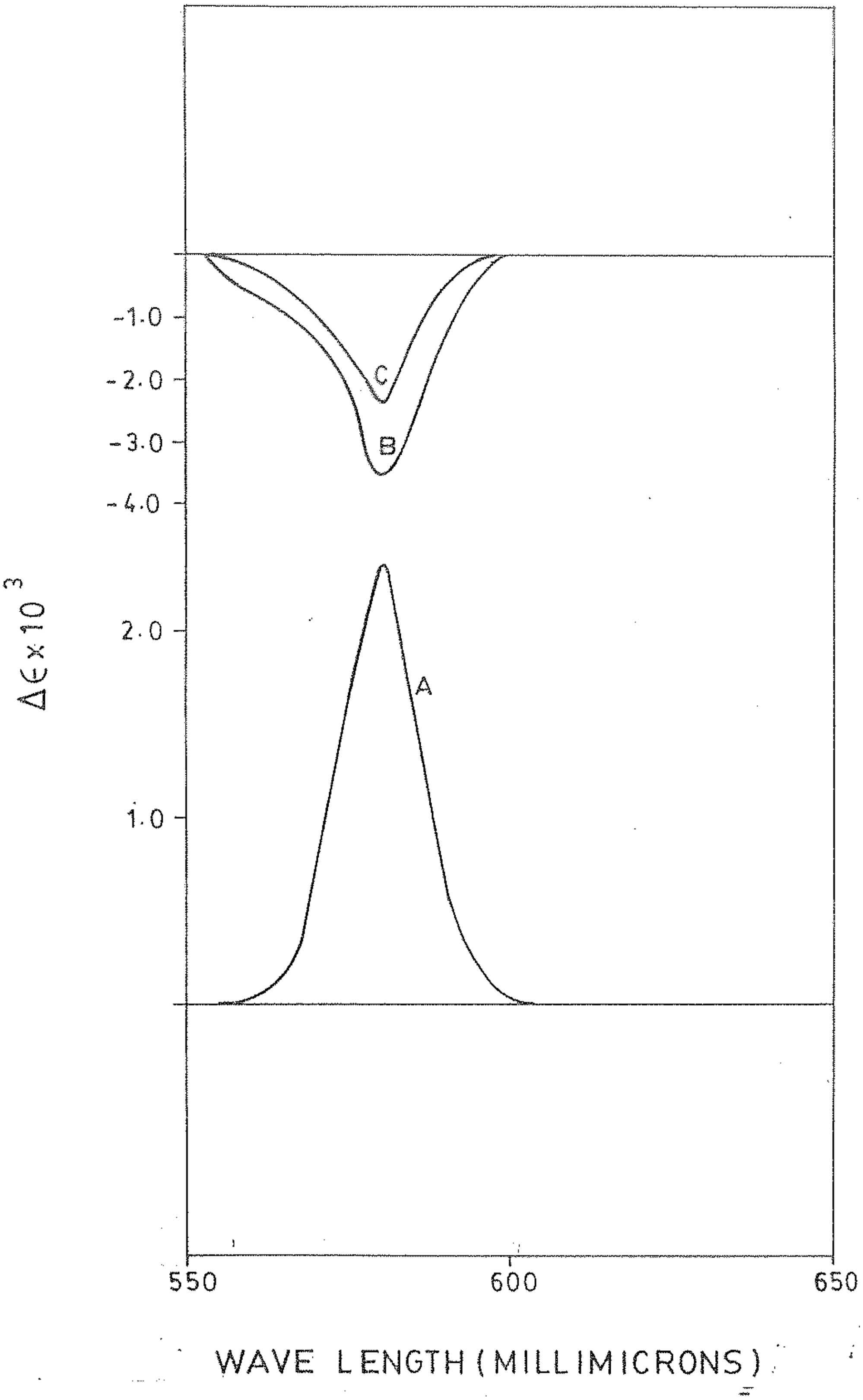


Fig. 11. Absorption spectrum (A) of [Nd (EDTA)$^{=}$] and Circular Dichroism Spectra of [Nd(EDTA)$^{-}$] (0.2 M) in presence of 0.8 M L (+)-Taric Acid (B) and 0.4 M (-)-Cinchonidine HCl (C)

intensity of the CD band was increased by increasing concentrations of both the components in the system. When pH of the system was gradually increased, the Pfeiffer CD band positions remained unaffected up to pH 10. The intensity of CD band was slightly increased with increasing pH (Fig 12). Above pH 10, CD spectrum of this system was essentially that of Nd-(+)-tartrate complex Fig.13.

CD of this complex ion $[Nd(EDTA)]^-$ in presence of (-)-cinchonidine HCl also consists of a sharp weak negative band at 17,391 cm^{-1}, which is comprable to that obtained in presence of (+)-tartaric acid (Fig 11) The chiral environment substance (+)-α-methylbenzylamine HCl and (+)-histidine failed to induce Pfeiffer CD in $[Nd(EDTA)]^-$, $[Pr(EDTA)]^-$ or $[Pr(DTPA)]^{2-}$ ions. The observed Cotton band at 17,391 cm^{-1} in this system may be assigned to excitation of electron from a lower energy f_{xyz} orbital to a higher energy f_{x^3}orbital.

(f) CD Studies On $[Co(BPA)_3]^{2+}$:

In aqueous solution $[Co(BPA)_3]^{2+}$ ion in presence of ammonium-(+)-α-bromocamphorsulphonate and ammonium-(-)-10-camphor sulphonate showed small changes in rotation and so a weak Pfeiffer effect. The CD spectrum of this ion in presence of NH_4-(+)-α-BCS consists of a weak positive Cotton band at 18,348 cm^{-1} and a relatively stronger negative band at 21,505 cm^{-1}. A mirror image spectrum for this complex ion was obtained in

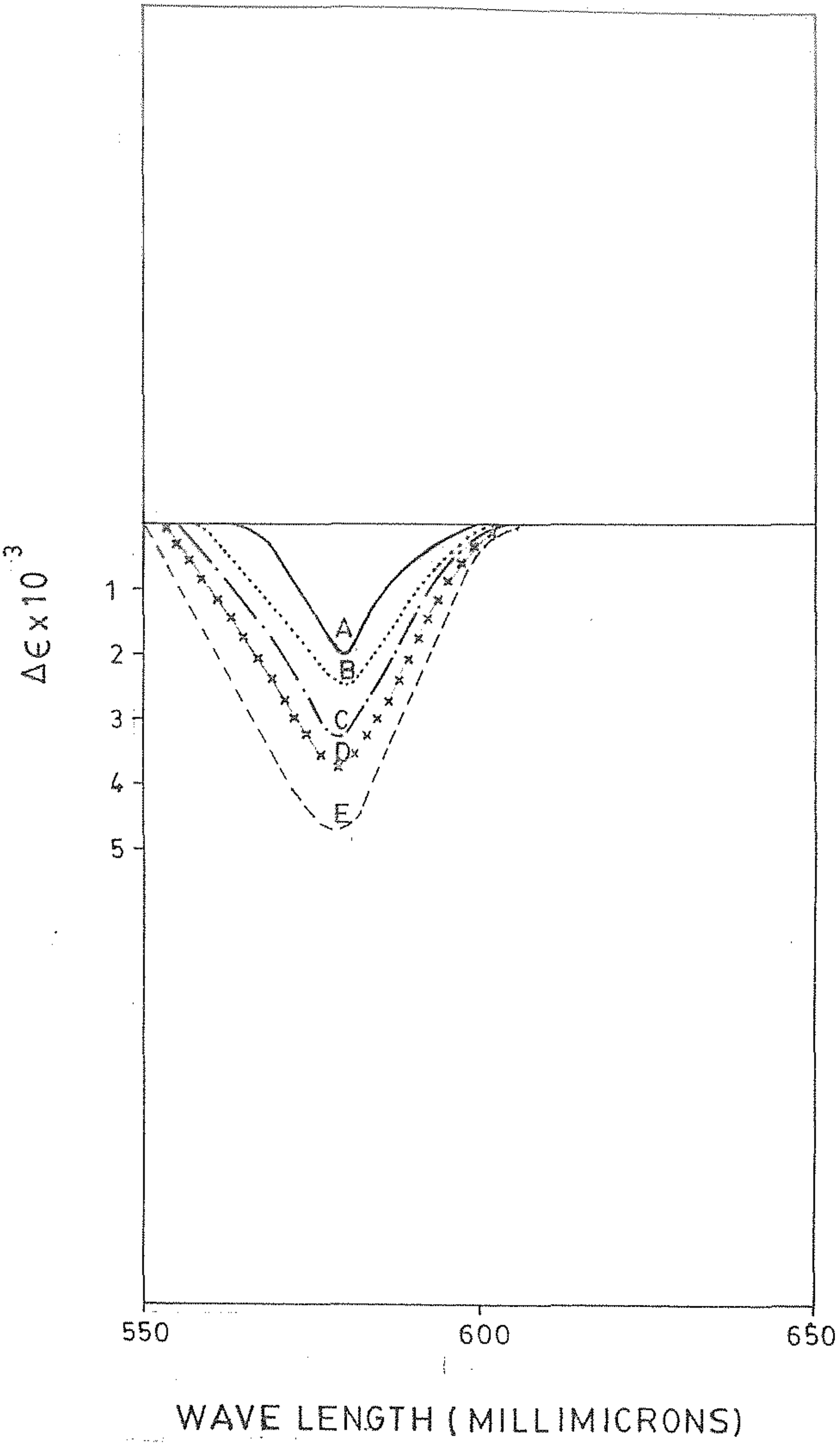


Fig. 12. CD Spectra of $[Nd(EDTA)]^-$ (0.1 M) in presence of (+)-T.A (0.4 M) at various pH (A)-2 (B) 4 (C) 6 (D) 8 (E) 10

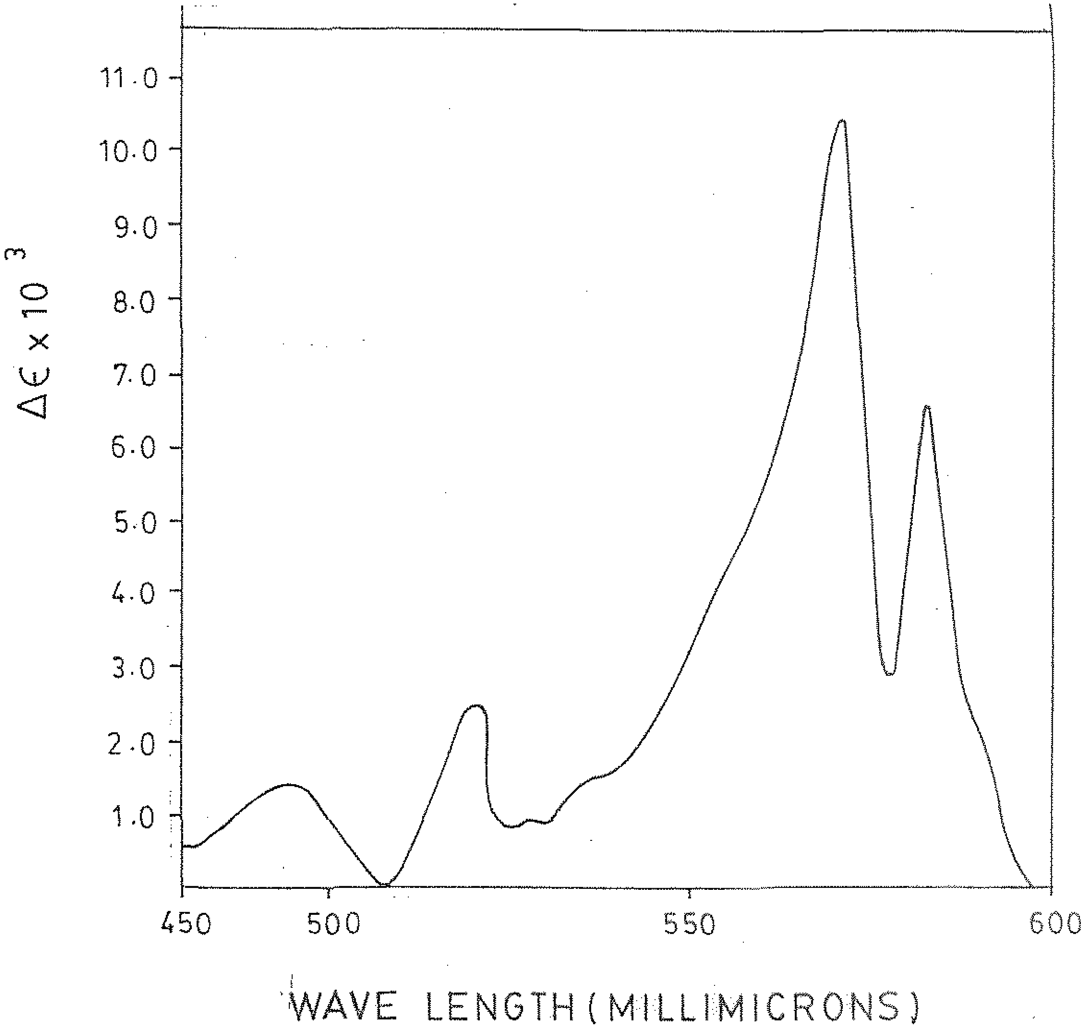


Fig. 13. CD Spectrum of a solution containing $NdCl_3$ and (+) T.A in molar concentration of 0.1 - 0.4 respectively, after adding excess of NaoH

presence of NH_4-(-)-10-camphorsulphonate (Fig 14), indicating that *leva* enantiomer of the complex was enriched in presence of this environment. The CD spectrum of this complex ion is typical of dissymmetric octahedral Co^{2+} complexes. The reported CD spectrum of (+)-[Co(phen)3]$^{2+}$ ion[72] in presence of various environment compounds consists of two weak positive Cotton bands at υ_1 18,609 cm^{-1} υ_2 20,200 cm^{-1} and a third stronger negative band at υ_3 22,320 cm^{-1}. The couplet of bands in CD spectrum of $[Co(BPA)_3]^{2+}$ are comparable in sign and magnitude to υ_2 and υ_3 of (+)-$[Co(phen)_3]^{2+}$.

This complex ion has D_3 symmetry and triply degenerate levels of octahedral symmetry will split to give $^4A_2$ and ^4E states to which electronic excitations may occur. A number of workers[73,74] have studied single crystal absorption spectra of complexes of this symmetry and assigned $^4A_2{}^4(T_{1g})$ as the ground state. These worker have detected considerable trigonal splitting in absorption bands due to low symmetry and assigned bands at 18,380 cm^{-1} to $^4A_2 \longrightarrow {}^4E$ transition and 19,000 cm^{-1} to $^4A_2 \longrightarrow {}^4A_1$ transition. The couplet of bands in $[Co(BPA)_3]^{2+}$may arise from excitation of electrons to ^4E and $^4A_1$ upper state of $^4T_{1g}(P)$ level in octahedral symmetry. The lower energy Cotton band 1 may be assigned to $^4A_2 \longrightarrow {}^4A_1$ transition, while higher energy band II may be due to $^4A_2 \longrightarrow {}^4E$ transition. Further the (+)-$[Co(BPA)_3]^{2+}$ ion enriched in presence of NH_4-(+)-α-BCS should have Δ absolute confi-

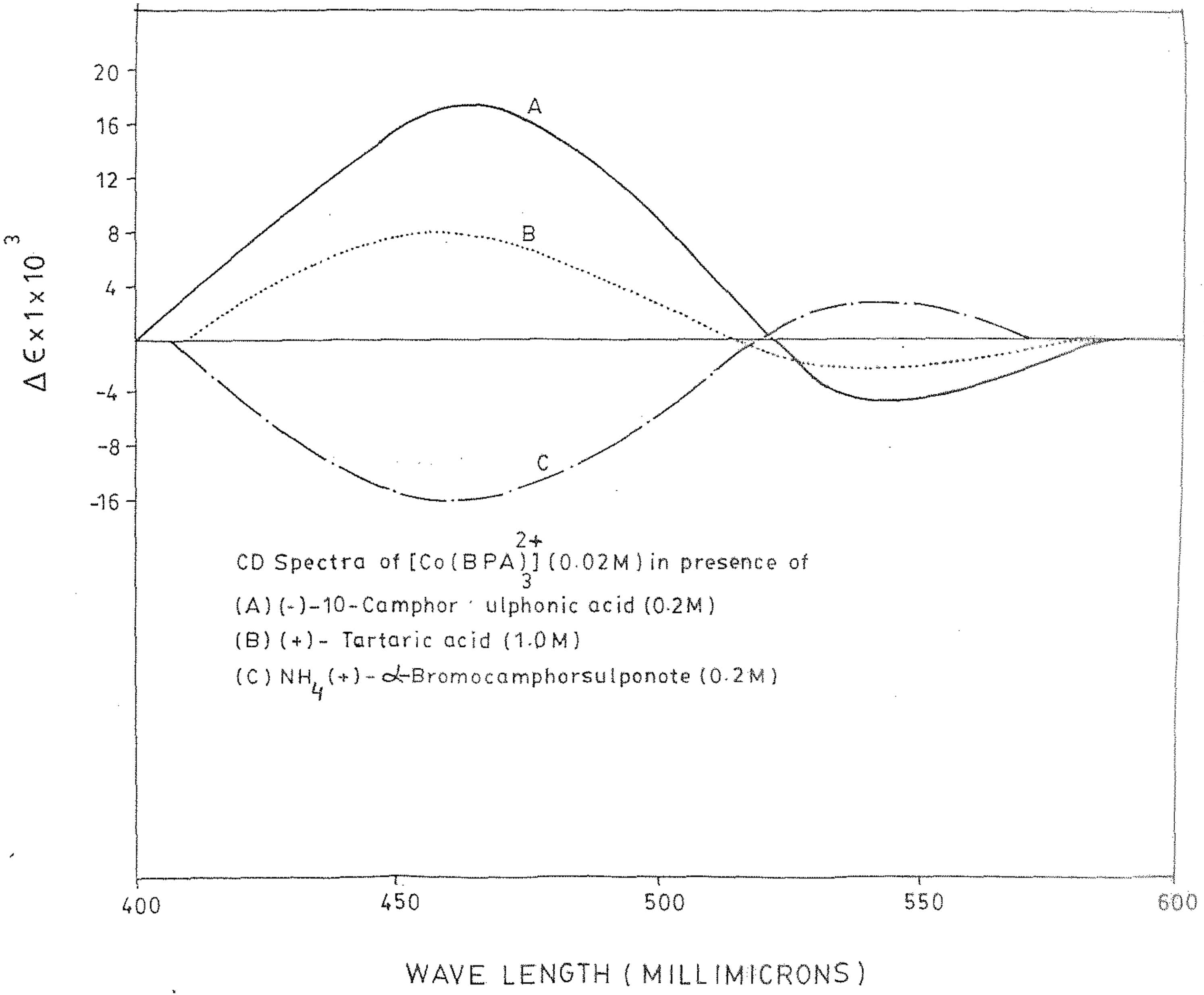


Fig. 14. CD spectra of $[Co(BPA)_3]^{2+}$ in Presence of Various Chiral environment substances in aqueous solution.

guration since Δ-$[Co(phen)_3]^{2+}$is enriched is presence of the same environment. It is observed that CD bands in $[Co(PBA)_3]^{2+}$ may be induced in presence of other chiral environment substances such as (+) tartaric acid, (-)-malic acid and (+)-ascorbic acid. These bands are slightly shifted towards lower frequency. The Pfeiffer effect was not induced in this complex ion in presence of (+)-tartaric acid when the two components were present in 1:4 molar ratio. However gradually increasing the concentration of (+)-tartaric acid in the system induced two Cotton bands, a negative band at 18,691 $cm^{-1}$and a positive band at 21,978 cm^{-1}. These bands may be due to outer sphere complexation of the environment substance as observed in $[Co(NH_3)_6]^{3+}$-(+)T.A[72]or $[Co(en)_3]^{3+}$-(+)T.A systems.[10] In this case outer sphere complexation seems unlikely because nitrogen atoms coordinated to metal ion are part of pyrdine ring and cannot participate in hydrogen bonding with (+)-tartrate ion, commonly accepted as the mechanism of outer sphere complexation. The Pfeiffer effect studies in $[Co(BPA_3)]^{2+}$ ion in presence of lithium -(+)-tartrate revealed that increased concentration of the environment in the system decreased the molar ellipticity of the CD bands. The CD spectrum of a system containing $[Co(BPA)_3]^{2+}$ and excess of Li_2((+)-tart) consists of several Cotton bands similar to that of $[Co((+)tart)_3]^{3-}$ ion. When (-)-malic acid was used as an environment in $[Co(BPA)_3]^{2+}$ system, no Cotton bands were observed immediately after mixing the components. However very strong well defined couplet of bands were developed after 24 hours. The CD spectrum of $[Co(BPA)_3]^{2+}$ ion in presence of (-)-malic acid consists of a negative Cotton band at 17,636 cm^{-1} and a positive band at 20,000 cm^{-1}. The magnitude of molar ellipticity and band positions are markedly affected upon increasing concentration of (-)-malic acid in the system. The CD spectrum of this ion in presence of (+)-ascorbic acid also consists of a strong positive Cotton band at 18,018 cm^{-1} and a second negative Cotton band at 21,978 cm^{-1}. The magnitude of ellipticity in this system suggests that (+)-ascorbic acid has partially displaced the BPA ligand in the complex.

It is apparent from the preceding discussion that $[Co(BPA)_3]^{2+}$ ion is kinetically very labile and bipyridylamine is rapidly displaced by relatively weaker ligands such as (+)-tartrate, (-)-malate and (+)-ascorbate ions, forming complexes of variable compositions such as $[Co(BPA)_{3-n}(L)]^{n+}$(n=1-3) in these solution systems. The interaction of chiral environment substances with the $[Co(BPA)_3]^{2+}$ ion is indicated by appearance of strong CD bands.

(g) CD Studies on $[Cu(ampy)_2]^{2+}$:

The CD spectrum of aqueous solution of $[Cu(ampy)_2]^{2+}$ in presence of NH4-(+)-α-BCS consists of a weak broad positive Cotton band at 17,857 cm^{-1}, while that in presence of

NH_4-(−)-CS has a mirror image spectrum. (Fig 15). The complex is a low symmetry (C_2) distorted species, which has unidimensional energy states. The extreme distortion of octahedron leads to square planar, four coordinated complexes. The broad positive Cotton band observed in presence of NH_4-(+)-α-BCS may be assigned to excitation of electrons to B upper state (d_{xz} or $d_{yz} \longrightarrow d_{z}2$).

A number of workers have reported absorption spectra of low symmetry copper (II) complexes and assigned a band 17,100-17,800 cm^{-1} to a similar transition.[75,76] It may be assumed that (+)-cis$[Cu(ampy)_2(H_2O)_2]^{2+}$ enriched in presence of NH_4-(+)-α-BCS has Δ absolute configuration, while levo enantiomer of this ion enriched in presence of NH_4-(−)-CS has Λ absolute configuration around the metal ion.

These studies reveal that CD spectra of Pfeiffer systems containing racemic metal complexes and chiral environment compounds may be utilized for assigning electronic transitions and absolute configurations of ligands around metal ions.

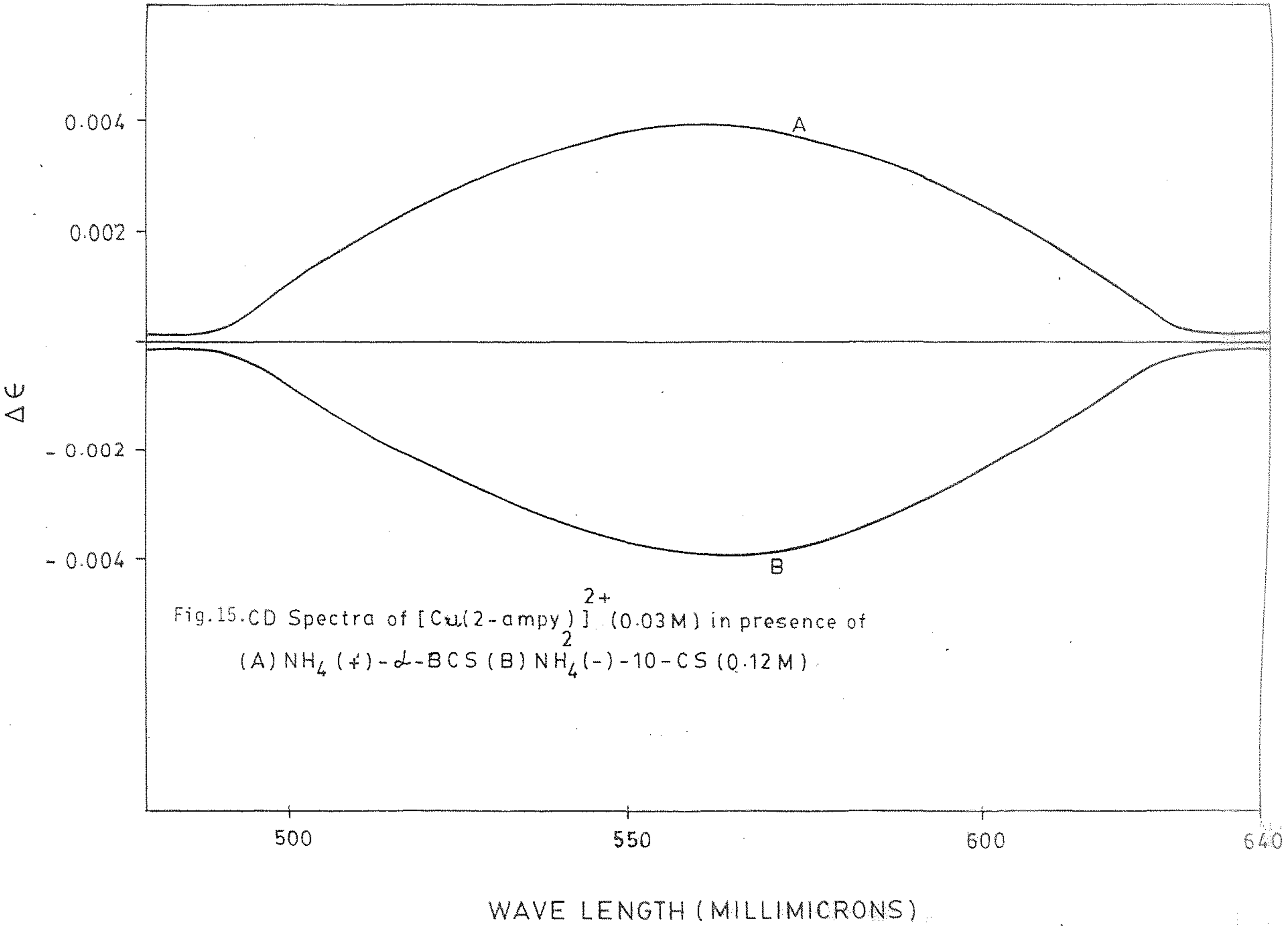


Fig.15. CD Spectra of $[Cu(2\text{-}ampy)_2]^{2+}$ (0.03M) in presence of (A) NH_4 (+)-α-BCS (B) NH_4(-)-10-CS (0.12M)

CHAPTER VII

CD STUDIES OF VANADIUM (III) COMPLEXES

The Pfeiffer effect studies in $[V(AA)_3]^{3+}$ (AA=phen or bpy) have never been reported. Therefore attempts were made to synthesise tris complexes of vanadium(III) with 1,10-phenanthroline and 2,2-bipyridyl. When solid ligands were mixed with aqueous solutions of vanadium(III) chloride and stirred, a deep purple coloured complex was formed in solution. Dwyer and coworkers[77] suggested the empirical formula as $[V(OH)(phen)_2)]^{2+}$ to the purple complex and proposed a dimeric structure. The sulphate and perchlorate salts of this complex are sparingly soluble in water and stable in air. However in aqueous solutions they are slowly oxidized to a tetravalent oxovanadium complex cation. The same purple complex may be obtained in crystalline form by reacting the components in non aqueous solvents such as methanol or DMF, or by fusion of the solid metal salt with the ligand in appropriate proportions. However these complexes are easily hydrolyzed in water.

Recently Shah et al.[59] reported that the purple complex is dimeric as $[(phen)_2V(\mu\text{-}OH)_2V(phen)_2]^{4+}$ with absorption maxima at 15,625 cm^{-1} and 19,047 cm^{-1}. Similar dimeric complexes of vanadium (III) with 2,2-bipridyl have also been reported by these workers. Stephen et al.[61] obtained the bipyridyl complexes of V(III) in crystalline form and suggested a binuclear structure to this complex in solid state. It was revealed from X-ray diffraction method that the two octahedra are joined through oxygen bridges and crystals of this complex has a C_2 axis passing through the bridging oxygen. The solution of this complex ion consist of very intense charge transfer absorption bands at 16,025 cm^{-1} and 18,939 cm^{-1}.

The binuclear vanadium(III) complexes with phen and bipy ligands were synthesised by mixing methanol solutions of vanadium(III) chloride and the ligand under nitrogen atmosphere, or by mixing aqueous solution of vanadium(III) choloride and the ligands, and by Stephen's method. The complexes prepared by all of these methods showed same absorption spectra in aqueous solution. The CD spectra of these complex ions in presence of various chiral environment substances were also similar. Therefore it was assumed that the same dimeric complex ion i.e. $[(AA)_2V(\mu\text{-}OH)_2V(AA)_2]^{4+}$ (where AA=1,10-phenanthroline or 2,2-bipyridyl) was present, when complexes prepared by any of these methods were dissolved in aqeous solution. When these complexes were dissolved in solutions of various environment substances large changes in optical rotation of the environment substances were observed in certain cases. The Chiral environment substances like NH_4-(+)-α-bromocamphorsulphonate and (-)-cinchonidine.HCl did not induce the Pfeiffer effect in these complexes. However a small change in optical rotation of (+)-ascorbic acid was observed in presence of either of the two complexes. As concentration of (+)-ascorbic acid was increased in these systems, appreciable changes in rotations were observed.

The CD spectra of these two complex ions in presence of (+)-ascorbic acid (as shown in Fig. 16) revealed a broad positive Cotton band at 18,868 cm^{-1} very close to the second absorption band of these complexes.Since these complexes have dark colours due to charge transfer bands in visible region, concentration of these complexes could not be increased above certain limits and small changes in molar ellipticity values were obtained.

The CD spectra of both of these complex ions in presence of (+)-tartaric acid consist of a couplet of oppositely signed Cotton bands. The first positive Cotton band is present in the region 16,949-17,544 cm^{-1}, whereas the second negative band is observed between 20,408-21,052 cm^{-1}. The CD spectra of both the complex ions are similar to each other in every detail with a slight difference in the wavelength of maxium absorption (Fig. 17,18). The CD spectrum of $[V_2(bpy)_4(\mu\text{-OH})_2]^{4+}$ ion in presence of (-)-malic acid also consist of couplet of bands, a negative band at 20,618 cm^{-1} and second possitive band at 17,391 cm^{-1}. The ellipticity of these Cotton bands is relatively smaller than that observed in presence of (+)-tartaric acid.

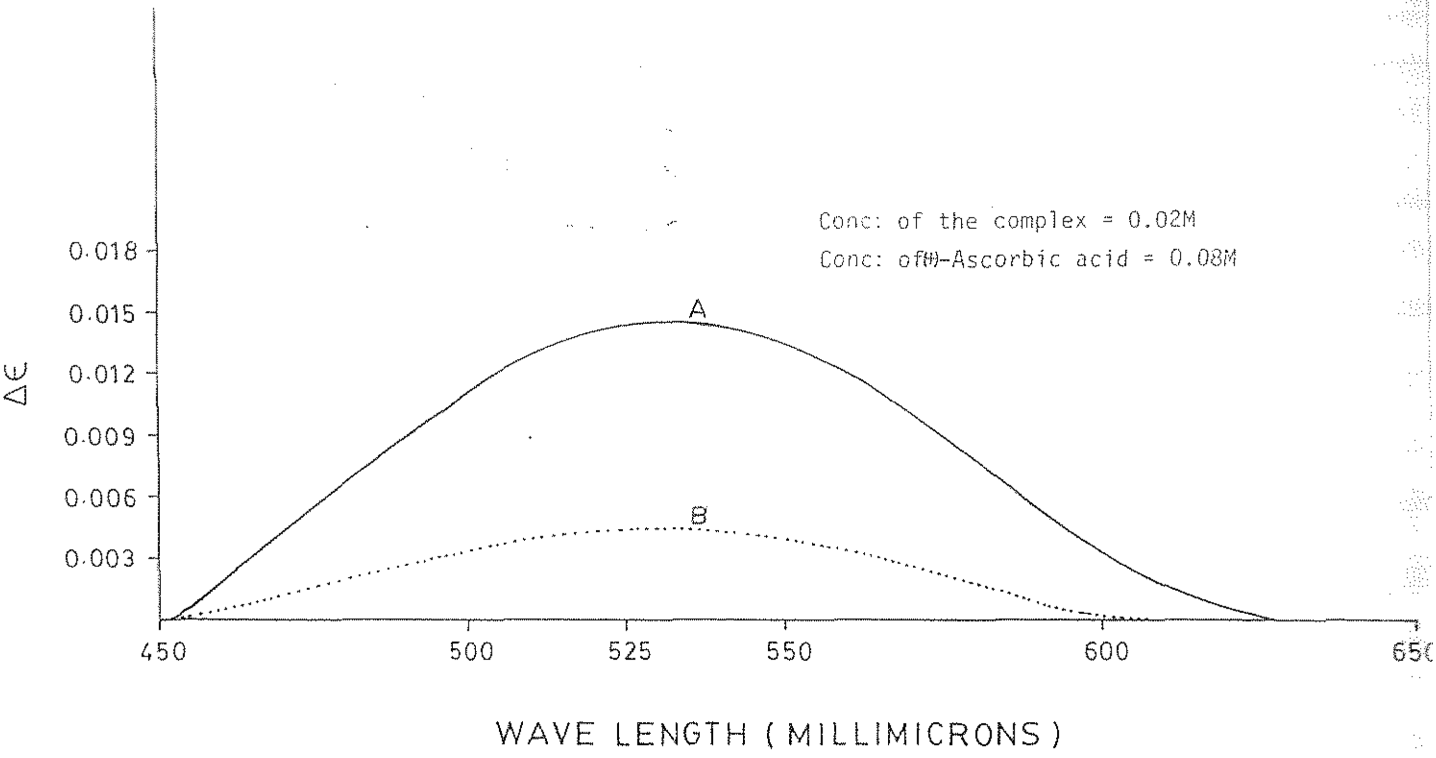


Fig. 16. CD Spectra of $[V_2(phen)_4(\mu\text{-}OH)_2]^{4+}$ and $[V_2(bpy)_4(\mu\text{-}OH)_2]^{4+}$ in Presence of (+)-Ascorbic Acid.

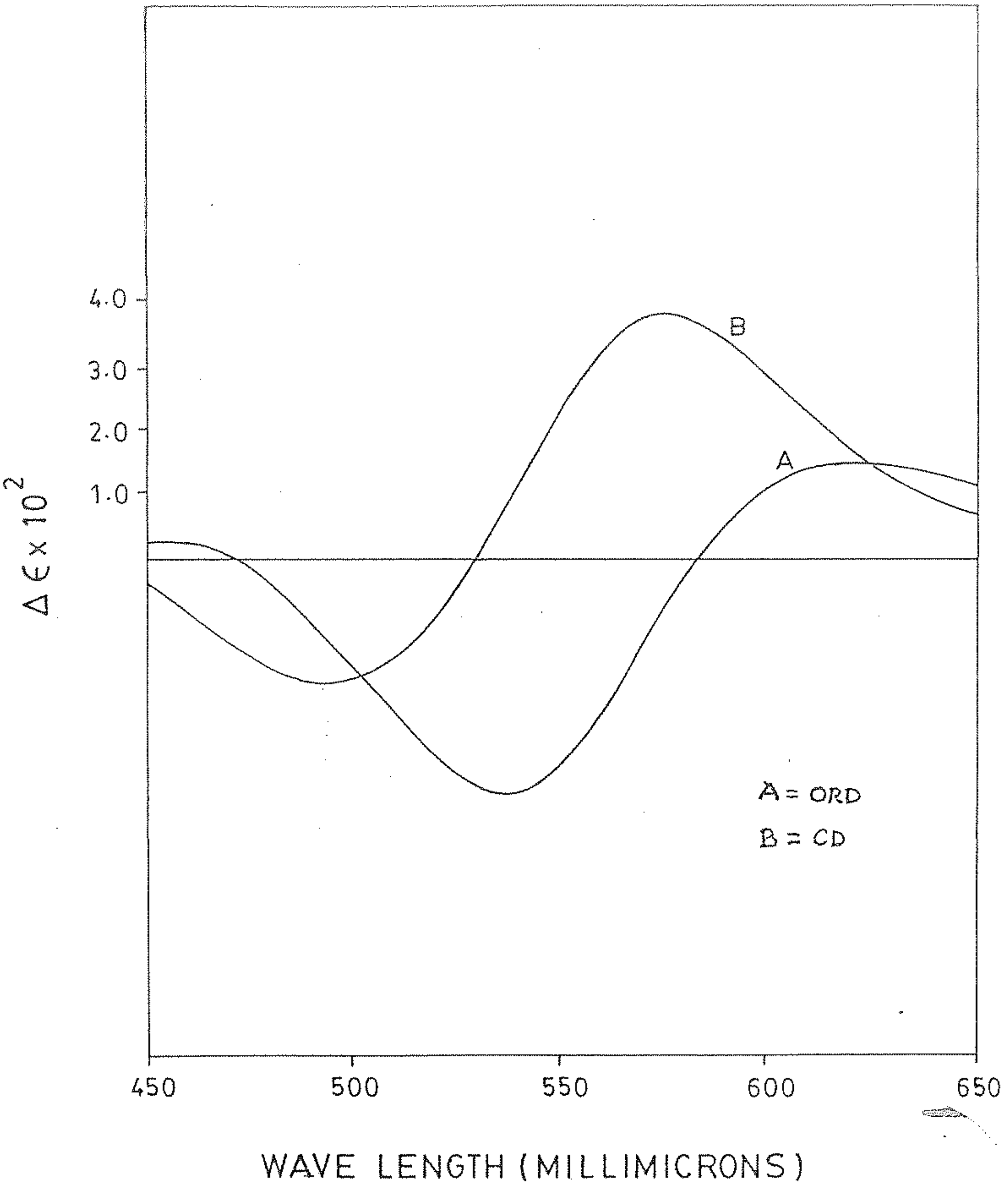


Fig. 17. CD and ORD Spectra of $[V_2(phen)_4(\mu\text{-}OH)_2]^{4+}$ in Presence of (+)-Tartaric Acid.

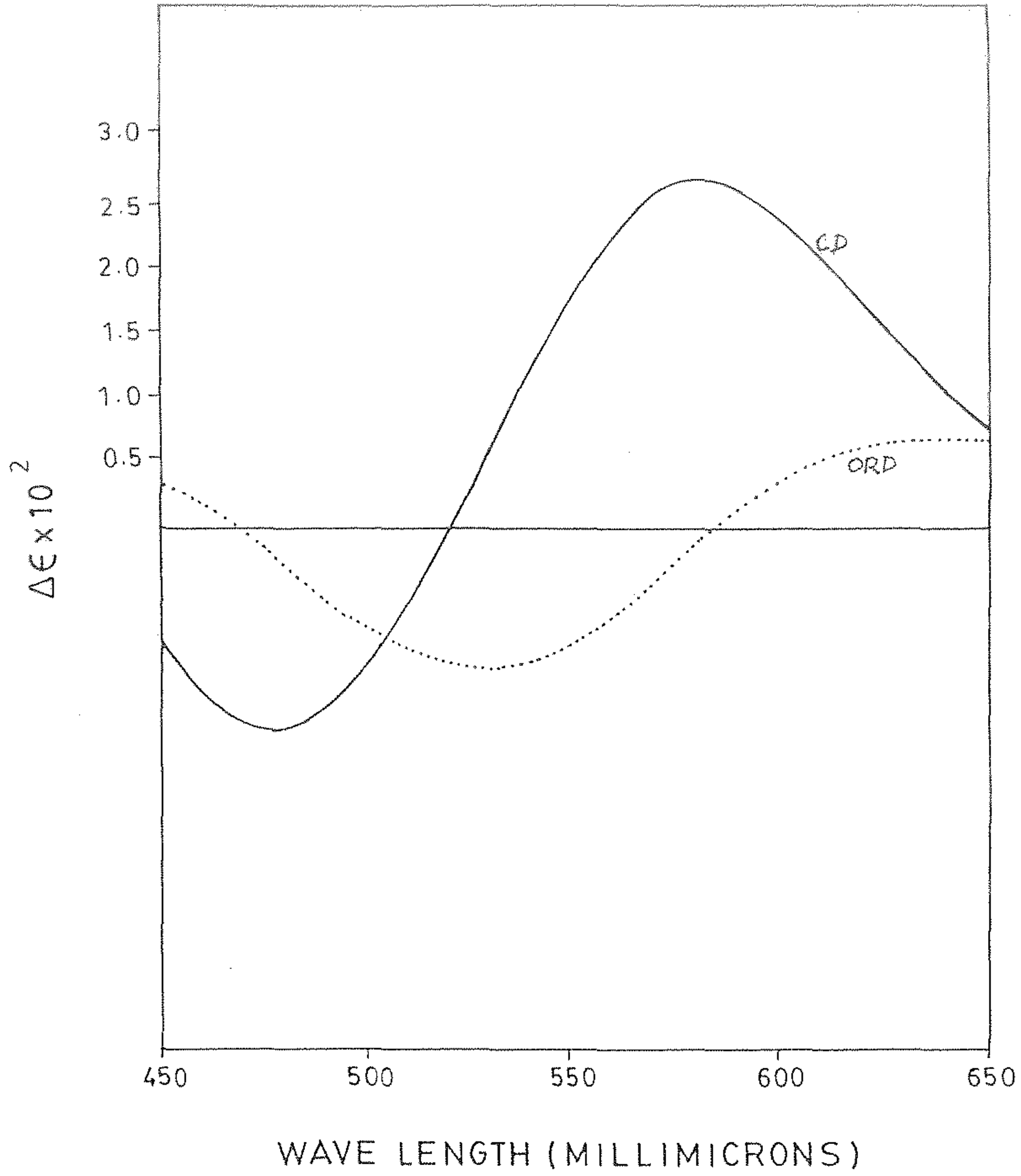


Fig. 18. CD and ORD Spectra of $[V_2(bpy)_4(\mu\text{-}OH)_2]^{4+}$ in Presence of (+)-Tartaric Acid.

(a) Effect of Change of Concentration of Chiral Environment:

When concentration of (+)-tartaric acid was gradually increased in the system keeping that of complexes constant, the Cotton band intensity was gradually decreased. This is contrary to the expected increase in band intensity. When excess of (+)-tartaric acid was present in the system the colour changed to light brown indicating the replacement of phen or bpy ligands by (+)-tartaric acid. This solution was changed to dark green upon keeping it for several days, perhaps due to oxidation of V(III) to VO^{2+} ion. CD of this oxidized solution was similar to that of a solution containing VO^{2+}, phen and (+)-T.A in 1:3:2 molar ratio respectively. The effect of increasing concentration of (+)-T.A is shown in Fig 19 and data is given in Table XII.

It is revealed from these studies that (+)-tartrate ion has gradually replaced the stronger phen or bpy ligands. This metal ion is labile and its complexes in solution exist in equillibrium as

$$[V_2(AA)_4(OH)_2]^{4+} \rightleftharpoons [V_2(AA)_{4-n}(OH)_2]^{4+} + nAA \quad (AA=1,10\text{-phen or } 2,2\text{-bpy}) \qquad (I)$$

$$[V_2(AA)_{4-n}(OH)_2]^{4+} + n(+)\text{-tartrate} \rightleftharpoons [V_2(AA)_{4-n}(tart)_n(OH)_2]^{n+} \qquad (II)$$

The second equillibrium may be shifted towards right side by increasing concentration of (+)-tartrate ion, ultimately giving

Table-XII(a) Effect of Increasing Concentration of (+)-T.A. on the Molar Ellipticity of $[V_2(bpy)_4(\mu\text{-}OH)(\mu\text{-}(+)\text{-}tart)]^{3+}$.

[Complex]	[(+)-T.A.]	$[\theta]^{25}_{575}$ deg.l.mol.cm^{-1}
0.02	0.02	1700
0.02	0.04	1150
0.02	0.06	1000
0.02	0.08	850
0.02	0.10	750

Table XII(b) Effect of Increasing Concentration of (+)-T.A. on the Molar Ellipticity of $[V_2(phen)_4(\mu\text{-}(+)\text{-}tart)]^{4+}$.

	[Complex]	[(+)-T.A.]	$[\theta]^{25}_{575}$ deg.l.mol.cm^{-1}
1.	0.02	0.02	1225
2.	0.02	0.04	1000
3.	0.02	0.06	825
4.	0.02	0.08	725
5.	0.02	0.10	675

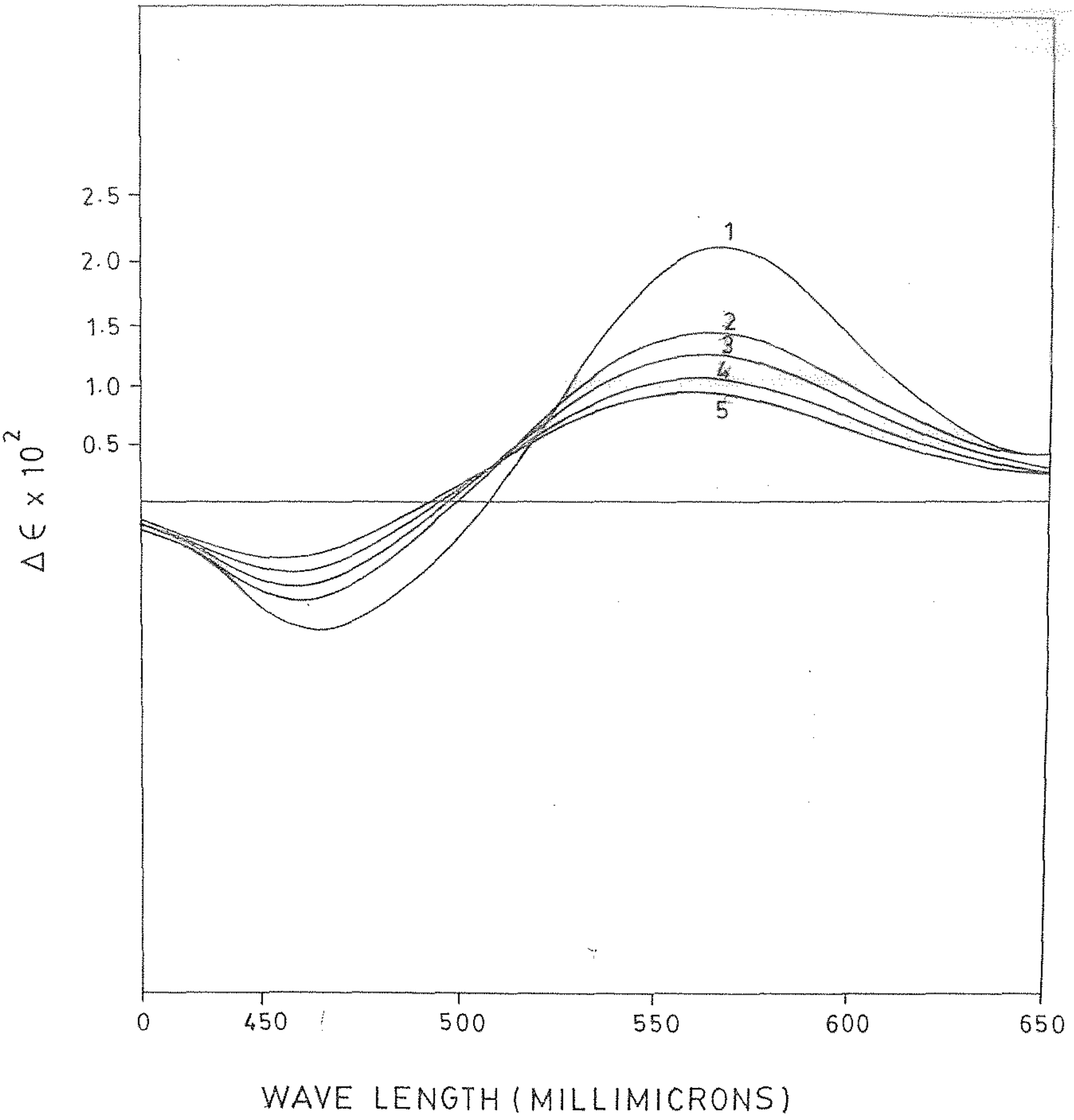


Fig. 19. Effect of Concentration of (+)-Tartaric Acid on the CD Band Ellipticity of $[V_2(phen)_4(\mu\text{-}(+)\text{-tart})_2]^{4+}$ in Aqueous Solution.

brown solution due to a mixed ligand complex $[V_2(\mathrm{phen})_{4-n}(\mathrm{tart})_n]^{n+}$ which is slowly oxidized to that of tetravalent VO^{2+} ion.

(b) Effect of Increasing Concentration of the Ligand:

Since purple solution of the complex ion is formed upon mixing the metal ion with the ligand, which gives a distinct CD spectra in presence of (+)-tartaric acid, it was considered appropriate to investigate the effect of increasing concentration of the ligand in these systems. A series of solutions of varying concentrations of 1,10-phenanthroline and constant concentration of V(III) ion and (+)-tartaric acid were prepared and their CD spectra were recorded. The data is given in Table XIII. The intensity of both Cotton band gradually increases with increasing conentration of the ligands. The Cotton band intensity is maximum at 1:9 metal to ligand ratio. Further increase in concentration of the ligand caused slight decrease in the band intensity. A linear plot was obtained when the ligand ratio was plotted against ellipticity at the band maxima (Fig. 20).

It may be inferred from these studies that the complex $[V_2(AA)_4(\mu\text{-}OH)_2]^{4+}$ ion in solution is in equillibrium with its components as given earlier (I). When ratio of the ligand is increased in the system, the equillibrium is shifted towards left and the concentration of the undissociated dissymmetric

Table XIII Effect of Concentration of 1,10-Phenanthroline on the Molar Ellipticity of $[V_2(phen)_4(\mu\text{-}(+)\text{-tart})]^{4+}$(0.025M).

No.	Concentration of 1, 10-phen	[θ]deg.l.mol.cm^{-1}
1	0.025M	406
2	0.05M	933
3	0.075M	2029
4	0.10M	3653
5	0.125M	4465
6	0.150M	6088
7	0.175M	7712
8	0.20M	8929
9	0.225M	10147
10	0.250M	9984

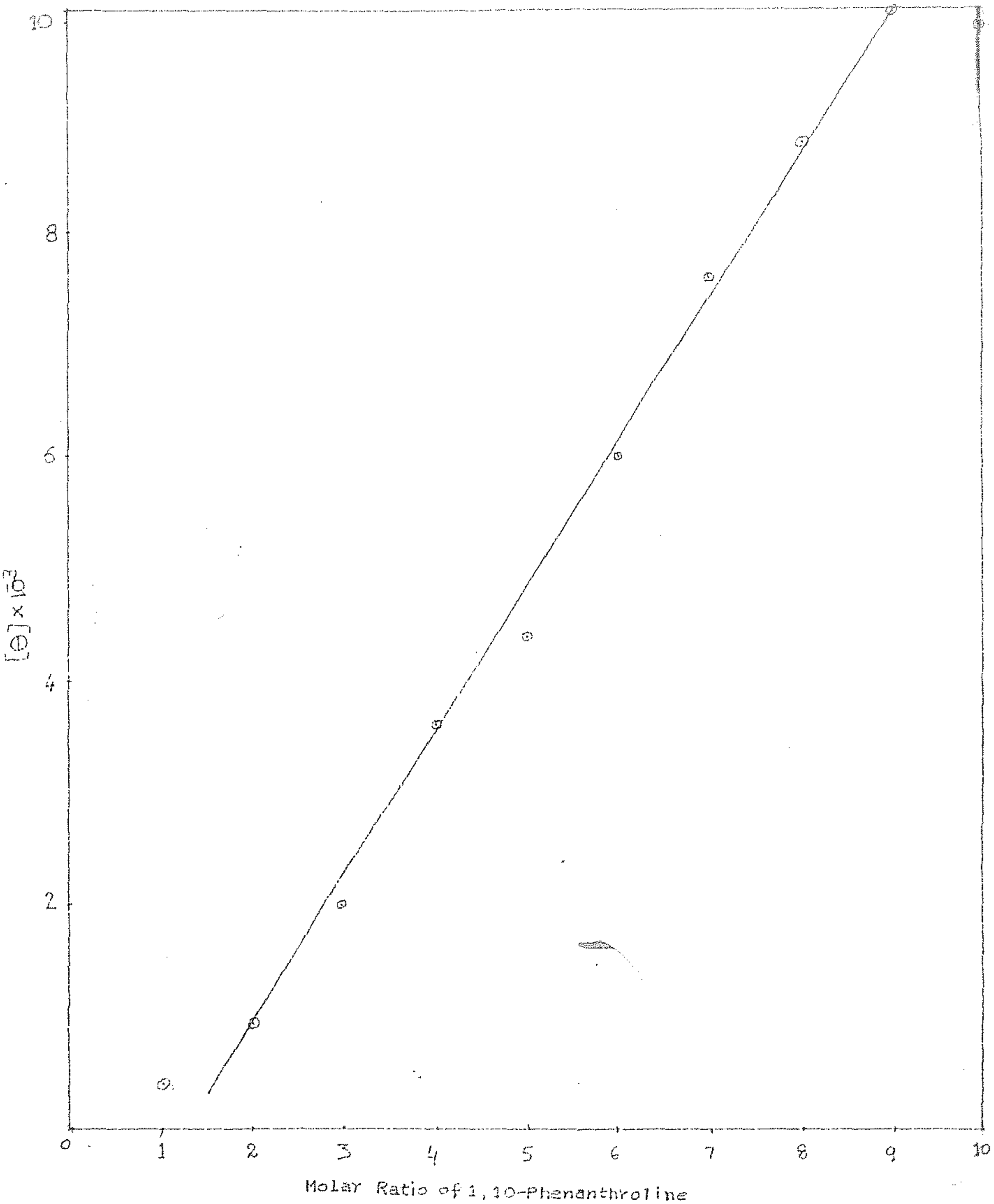


Fig. 20. Effect of Concentration of 1,10-Phenanthroline on the CD Band Ellipticity of $[V_2(phen)_4(\mu\text{-}(+)\text{-}tart)_2]^{4+}$ in Aqueous Solution.

complex A is increased, thus increasing the ellipticity at the band maxima. In presence of excess of the ligand (1:9), concentration of undissociated binuclear species is maximum (99.9 %). Further increase in concentration of the ligands in the system has no profound effect upon Cotton band ellipticity.

(c) Isolation of the Solid Perchlorate Complexes:

It was possible to isolate solid optically active purple species from the system containing $[V_2(AA)_4(\mu\text{-}OH)_2]^{4+}$ and (+)-tartaric acid, by adding sodium perchlorate solution. A purple complex was precipitated out in each case in presence of excess of perchlorate ion and separated. Elemental analyses of these complexes as perchlorate salts were obtained and probable stoichiometry was determined. The elemental analysis fits well in binuclear formula as $[(phen)_2V(\mu\text{-}(+)\text{-}tart)V(phen)_2](ClO_4)_4$ and $[(bpy)_2V(\mu\text{-}OH)(\mu\text{-}(+)\text{-}tart)V(bpy)_2](ClO_4)_3$

Analytical: For $[V_2(C_{48}H_{32}N_8)\ (C_4H_4O_6)](ClO_4)_4$

Calculated: C= 45.62 H = 2.63 N = 8.19 Cl = 10.37 % .

Found: C= 45.47 H = 3.06 N = 8.18 Cl = 9.17 % .

For $[V_2(C_{40}H_{32}N_8)(OH)(C_4H_4O_6](ClO4)3$

Calculated: C = 44.4 H = 3.13 N = 9.41 Cl = 8.94 %

Found: C = 43.85 H = 2.86 N = 9.59 Cl = 10.44 %

These elemental analysis of precipitated perchlorate complexes indicate that (+)-tartrate ion has entered the coordination sphere of V(III) ion replacing the bridging hydroxide. In $[V_2(phen)_4(\mu\text{-}OH)_2]^{4+}$ both hydroxide ions have been replaced by one (+)-tartrate ligand, while in $[V_2(bipy)_4(\mu\text{-}OH)_2]^{4+}$ only one OH has been replaced by (+)-tartrate ion. The presence of tartrate ion in these complexes is also indicated, by appearance of a reasonably strong band at 1734-1740 cm^{-1} due to uncoordinated carbonyl stretching vibration in their infrared spectra.

The precipitated perchlorate salts of these complexes were converted into water soluble chloride through anion exchange resin (Amberlite-IRA-400). The CD spectra of these solutions were similar in every detail to those obtained in presence of (+)-tartaric acid for these complex ions. The Cotton band ellipticity of these systems decreased with time and ultimately the purple solutions were changed to dark green, indicating oxidation of V^{3+} ion to VO^{2+} ion. The CD spectra of these oxidized complexes are different from that of $[VO((+)\text{-}tart)_2]^{2-}$ system as reproduced in Fig. 21.

The loss of optical activity in these purple complexes was taken from the rate of decrease in ellipticity of Cotton band with time. Therefore CD spectra of these system were measured after regular intervals of time (Fig. 22). A plot of molar ellipticity at band maxima as a function of time was prepared as shown in Fig. 23. This plot is a stright line and is quite different from the regular racemization plots of Ist order kinetics. The loss of optical activity in these systems

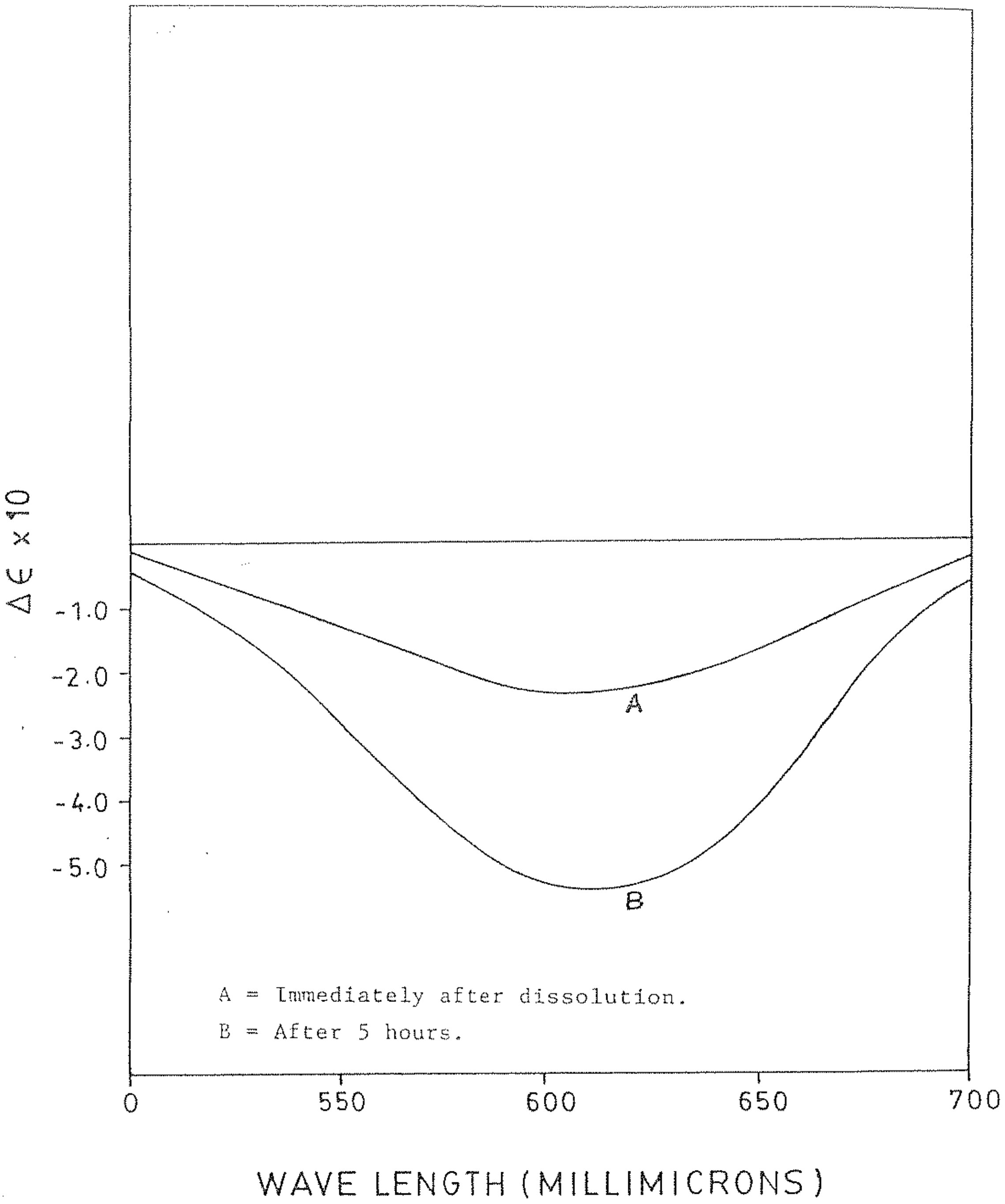


Fig. 21. CD Spectra of the Mononuclear Vanadium Complexes

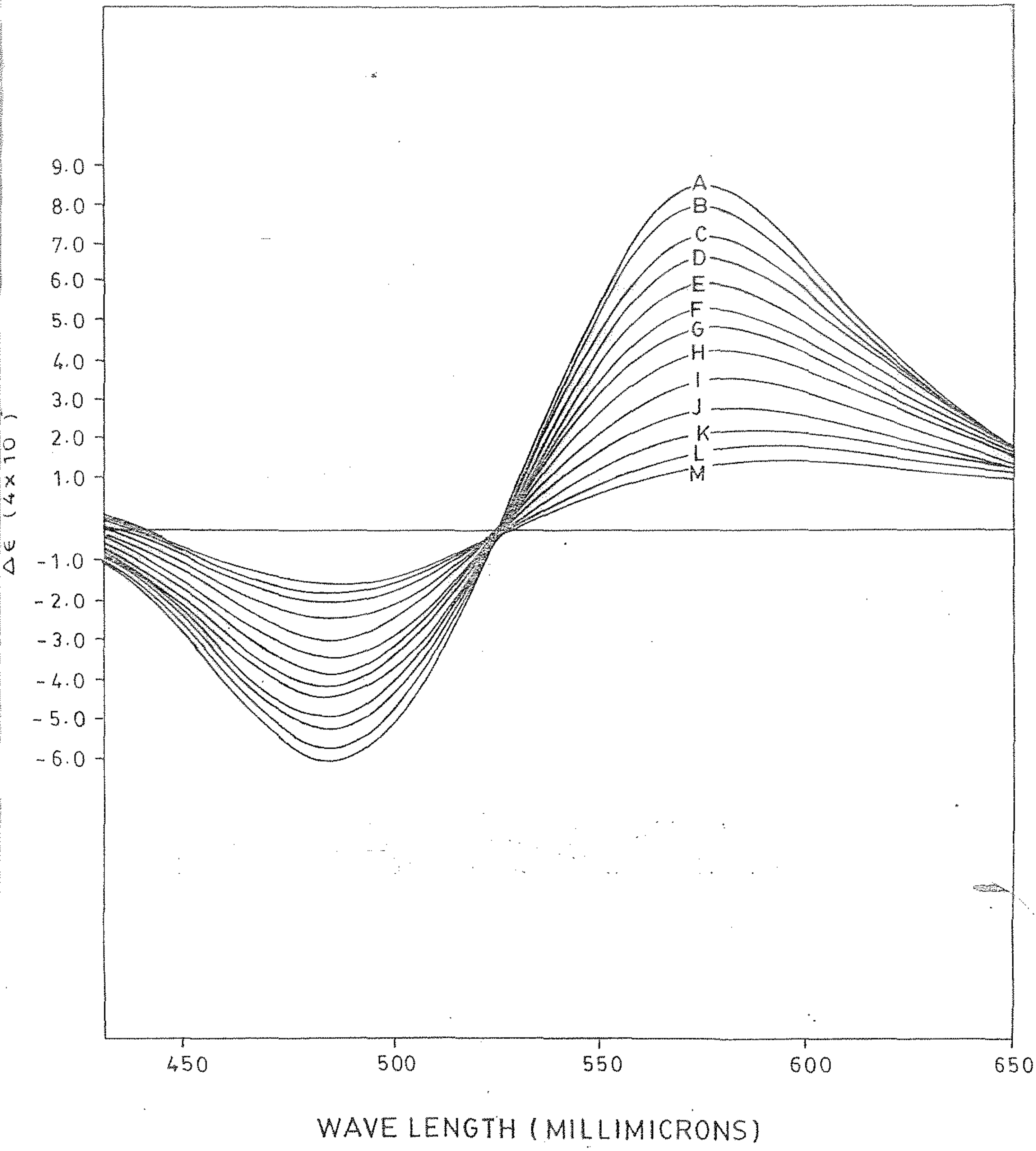


Fig. 22. CD Spectra of $[V_2(phen)_4(\mu-(+)-tart)_2]^{4+}$ in Aqueous Solution Recorded from A - M, After each 30 minutes.

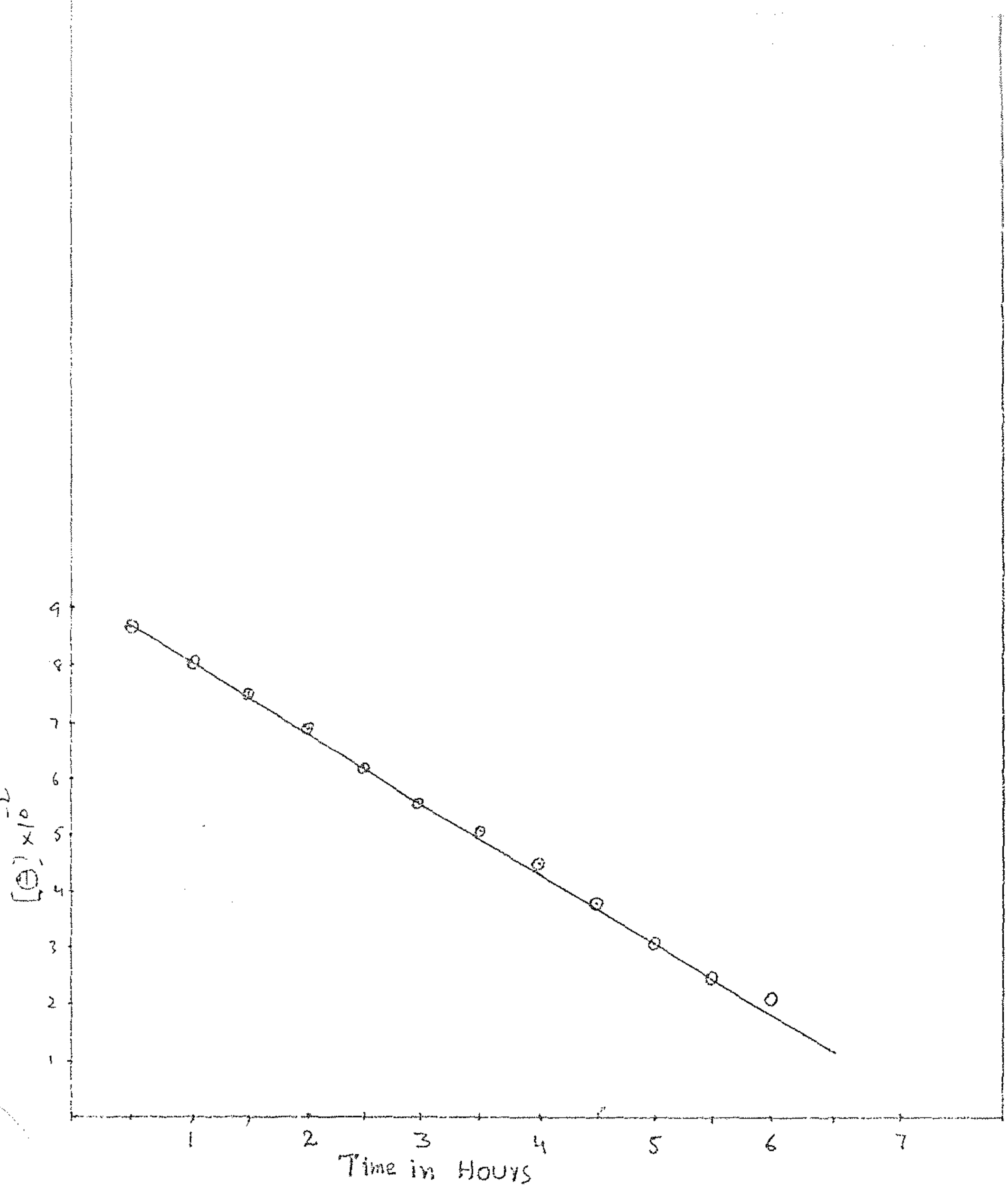


Fig. 23. Oxidation of $[V_2(phen)_4(\mu\text{-}(+)\text{-}tart)_2]^{4+}$ into $[VO(phen)_2Cl]^+$ in Aqueous Solution.

cannot be solely from racemization. It seems that oxidation of V^{3+} complex into that of VO^{2+} followed by conversion into monomeric cis-$[VO(phen)_2Cl]^+$ may be responsible for these Circular Dichroism changes. Formation of $[VO(phen)_2OH_2]^{2+}$ is indicated with gradual appearance of a negative Cotton band at 16,393 cm^{-1} in the system. The half life of this process in case of $[V_2(phen)_4(\mu\text{-}OH)_2]^{4+}$ is 3.5 hours, while for $[V_2(bpy)_4(\mu\text{-}OH)_2]^{4+}$ it is 1.5 hours.

(d) Effect of time on Band Ellipticity:

The ellipticity of Cotton bands in solution containing $[V_2(AA)_4(\mu\text{-}OH)_2]^{4+}$ and (+)-tartaric acid was gradually decreased with time. The purple colour of the complex was slowly changed to brown and then green, indicating oxidation of V^{3+} complex to that of VO^{2+} ion. The purple colour of aqueous solutions containing $[V_2(bpy)_4(\mu\text{-}OH)_2]^{4+}$ and (+)-tartaric acid was oxidized to green vanadyl complex ion at a faster rate while oxidation of $[V_2(phen)_4(\mu\text{-}OH)_2]^{4+}$ occured at relatively slower rate under similar conditions. CD spectrum of the green solution (as shown in Fig.21) consist of a strong negative Cotton band at 16393 cm^{-1} with molar ellipticity of 84.56 deg cm^{-1}l $mole^{-1}$. This CD spectrum is different from that of simple VO^{2+}-tartrate and VO^{2+}-phen-tartrate systems. The green complex ion formed in $[V_2(bpy)_4(\mu\text{-}OH)_2]^{4+}$ and (+)-tartaric acid solution was separated as perchlorate and analyzed. The elemental analysis of this green complex fits well in a monomeric complex as $[VO(bpy)_2Cl](ClO_4)$.

Analytical: For $[VO(C_{10}H_8N_2)_2Cl]\ (ClO_4)$

Calculated C = 46.71 H = 3.14 N = 10.89 Cl = 13.79 %

Found: C = 47.11 H = 3.61 N = 10.76 Cl = 14.02 %

Brand et.al.[61] have already synthesized this emarald green vanadyl complex of composition $[VO(bpy)_2Cl](ClO_4)$ and determined its structure by X-ray diffraction method. These workers have assigned a cis arrangement of oxo and Chloro ligands around the metal ion which is dissymmetric and should exist as *dextra* and *leva* eantiomers.

The emerald green perchlorate complex was again converted into a water soluble chloride form. CD spectrum of the green solution consists of a broad negative band at 16,393 cm^{-1}. The Cotton band ellipticity of this solution increased with time and became constant after 5-6 hours. After this time the green solution is stable for indefinite period and no further changes either in CD or colour were observed over several weeks. These changes in ellipticity of Cotton band may be attributed to a hydrolysis of coordinated chloride ion to form an aquo complex which is completed in 5-6 hours. After this time no further change in composition of the complex or oxidation of the metal ion was possible.

It was also observed that the solid $[V_2(AA)_4(\mu\text{-}(+)\text{-tart})](ClO_4)_4$ changed to a green moiety in sample bottles after 1-2 months. These green perchlorate salts when converted to water soluble chloride have CD spectra similar to those of oxidized VO^{2+} complexes as shown in Fig. 21.

It may be inferred from the preceding observations that the optically active binuclear complex is slowly oxidized in solution as well as in solid state into a mononuclear species. In this process (+)-tartrate ion is released and an optically active mononuclear specias such as cis-$[VO(AA)_2Cl]^+$ ion is formed. The chiral (-)-cis-$[VO(AA)_2Cl]^+$ is completely hydrolyzed to form (-)-$[VO(AA)_2OH_2]^{2+}$ in aqueous solution in 5-6 hours. The mechanism of formation of the mononuclear complex is given in Fig. 24.

It is clearly demonstrated from this sequence of reactions that in solutions (+)-tartrate ion is coordinated as a bridge in these binuclear vanadium (III) complexes, which may be separated as $[V_2(phen)_4(\mu\text{-tart})](ClO_4)_4$ and $[V_2(bpy)_4(\mu\text{-OH})(\mu\text{-tart})](ClO_4)_3$. In solution these complexes oxidize to a green mononuclear form of vanadyl species which may be seperated as (+)-cis-$[VO(bpy)_2Cl](ClO_4)$ and (+)-cis-$[VO(phen)_2Cl]ClO_4$. In aqueous solutions these complex ions are hydrolyzed to form (+)-cis-$[VO(AA)_2(OH_2)]^{2+}$ ions.

The CD spectra of $[V_2(phen)_4(\mu\text{-}(+)\text{-tart})]^{4+}$ and $[V_2(bpy)_4(\mu\text{-OH})(\mu\text{-}(+)\text{-tart})]^{3+}$ consist of a positive band I at 17,391-17,543 cm^{-1} with molar ellipticity 830-1100 deg.l.mol^{-1}.cm^{-1} and negative band II at 20,408-20,833 cm^{-1} with molar ellipticity 500-600 deg.l.mol^{-1}.cm^{-1}. The absorption spectra

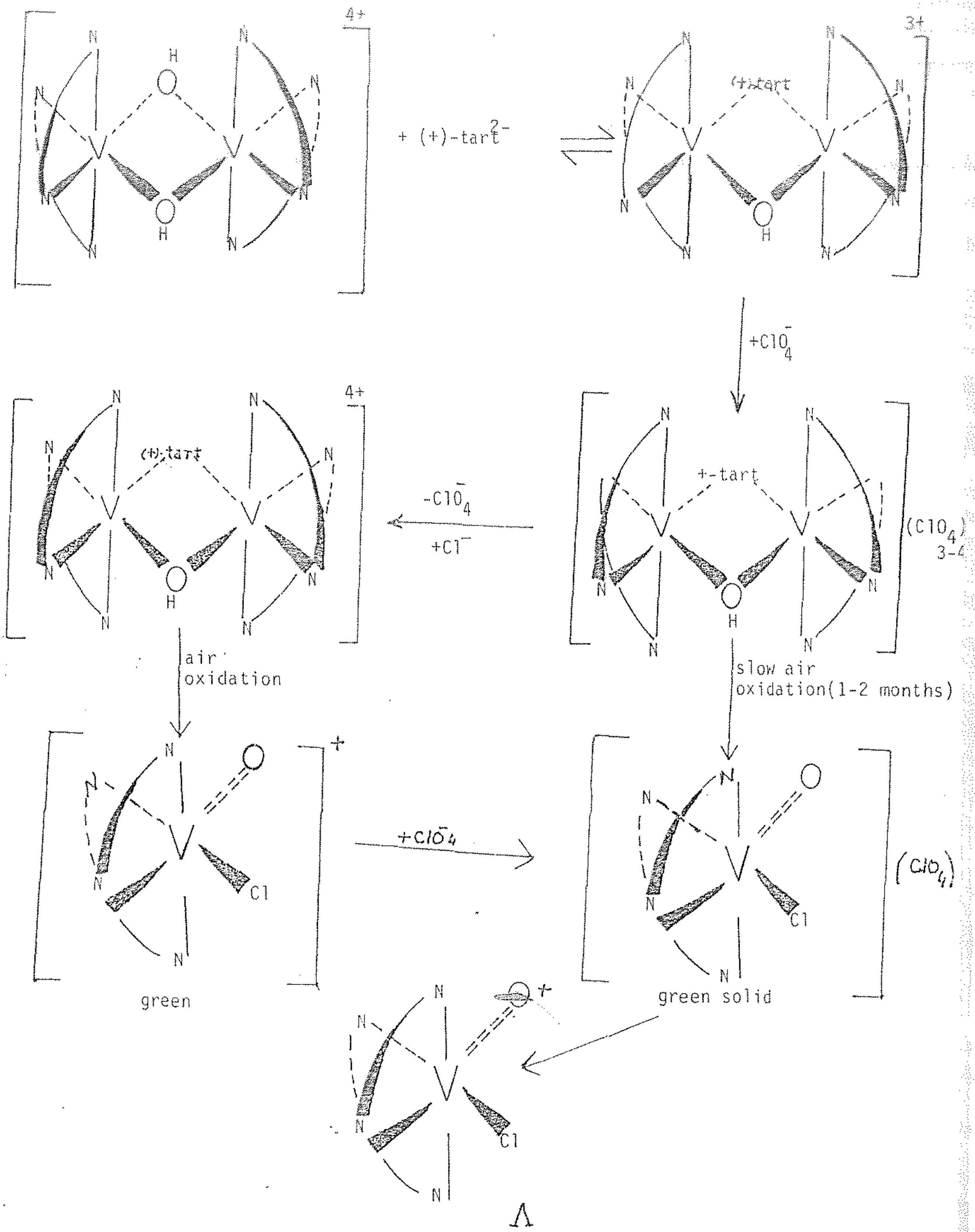


Fig. 24. Mechanism of Formation of the Mononuclear Vanadium Complexes.

of these two complex ions also consist of two very intense bands between 16,000-16,129 cm^{-1} and 19047-19230 cm^{-1}. These two bands are associated with very high values of extinction coefficient and molar ellipticity, indicating that they arise from charge transfer transitions. The molecular orbital energy level diagram of these system consist of low lying empty anti-bonding pi orbitals from unsaturated phen or bipy ligands apart from other sigma and pi bonding orbitals. Since these complexes have low symmetry (C_2), all energy levels are unidimensional. The higher energy negative Cotton band II in these system may be assigned to d(A) $\longrightarrow$ (Π^*),MLCT transition, while the lower energy positive Cotton band I may be assigned to $\Pi \longrightarrow$ d(A) LMCT transition. A number of workers have studied absorption spectra of bipyridyl complexes of bivalent Fe, Ru, Os and assigned bands between 18,052-22,300 cm^{-1} to d $\longrightarrow \overset{*}{\Pi}$, and 14,790-19,570 cm^{-1} to $\Pi \longrightarrow t_2g$ LMCT transition. The two Cotton bands in these complexes are in agreement with the reported absorption band assignments.

The CD of green mononuclear complex ion i.e. (+)-cis $[VO(bpy)_2Cl]^+$ consists of a negative Cotton band at 16,393 cm^{-1} with molar ellipticity of 250 deg.l.mole.cm.$^{-1}$ [illegible] The band position and its molar ellipticity values suggest that it arises from excitation of electrons within d orbitals and not from charge transfer transitions as for the binuclear V(III) complexes.

Table-XIV CD Spectral Data of Binuclear and Mononuclear Vanadium Complex Ions.

Complex Ion	CD Bands			
	Band-I		Band-II	
	ν(cm^{-1})	[θ]	ν(cm^{-1})	[θ]
$[(phen)_2V(\mu\text{-}(+)\text{-}tart)V(phen)_2]^{4+}$	16,949	+1100	20,408	-600
$[(bpy)_2V(\mu\text{-}OH)(\mu\text{-}(+)\text{-}tart)V(bpy)_2]^{3+}$	17,544	+830	21,052	-500
$(+)\text{-}[VO(phen)_2Cl]^+$	16,393	-250	------	----
$(+)\text{-}[VO(bpy)_2Cl]^+$	16,393	-250	------	----

Absorption spectra of a number of vanadyl complexes have been reported and assigned to various electronic transitions within d orbitals. Ballhausen et.al.[78] studied and interpreted absorption spectrum of $[VO(H_2O)_5]^{2+}$ (C_{4v}) suggesting the $d_{xy} < d_{xz}, d_{yz} < d_{x^2-y^2} < d_{z^2}$ ($b_2 < e < b_1 < a_1$) as energy order of d-orbitals in this system. These workers assigned three observed bands to electronic transitions as

I $b_2 \longrightarrow e^*$ $(^2B_2 \longrightarrow {}^2E)$ 10,300-14,820 cm^{-1}

II $b_2 \longrightarrow b_1^*$ $(^2B_2 \longrightarrow {}^2B_1)$ 11,909-17,360 cm^{-1}

III $b_2 \longrightarrow a_1$ $(^2B_2 \longrightarrow {}^2A_1)$ 15,500-25,000 cm^{-1}

Later workers used this electronic excitation pattern for assigning absorption bands in various low symmetry vanadyl complexes. Presently three absorption bands (observed in a variety of vanadyl complexes) have been assigned to these transition as indicated above.[79] The negative Cotton band at 16,393 cm^{-1} in (+)-cis-$[VO(bpy)_2Cl]^+$ and its hydrolyzed product is in the frequency region of aborption band II of other vanadyl complexes. This transition in low symmetry complexes should be dichroic as it is allowed by magnetic dipole selection rules. Therefore this Cotton band may be easily assigned to excitation of electrons from d_{xy} to $d_{x^2-y^2}$ obritals (i.e $^2B_2 \longrightarrow {}^2B_1$).

It is possible to correlate the absolute configuration of ligands around metal ion from these studies. Mason[80,81] has studied CD spectra of a number of metal complexes with 1,10-phenanthroline and 2,2-bipyridyl ligands using symmetry and exciton theory. He has correlated sign of Cotton band with absolute configuration, particularly in complexes of iron group (i.e. Fe^{2+}, Ru^{2+} and Os^{2+}) elements. These complexes are associated with deep red colour due to charge transfer absorption bands in visible region of the spectrum.

The present series of binuclear complexes of vanadium (III) have also charge transfer bands in visible region. Therefore CD spectra of these complexes may be compared with CD of dissymmetric complexes of Fe(II), Ru(II) and Os(II) with phen or bpy ligands. Further Λ absolute configuration of (-)-$[Fe(phen)3]^{2+}$ has already been determined by X-ray diffraction methods.[82]

Bosnich[83] has investigated absorption and CD spectra of (-)-cis-$[Ru(phen)_2(py)_2](ClO_4)_2$ and correlated its absolute configuration as 'Λ' on the basis of sign of Cotton bands arising from long axis polarized transitions of o-phenanthroline. The CD spectra of these binuclear complexes may be compared with that of (-)-$[Fe(bpy)_3]^{2+}$ and (-)-cis $[Ru(phen)_2(py)_2]^{2+}$ ions. The later two complexes have a mirror image CD spectra in the visible region of the spectrum to that of present series of complexes. Therefore both (+)-$[V_2(phen)_4$-

(μ-(+)-tart)]$(ClO_4)_4$ and (+)-[$V_2(bpy)_4(\mu$-OH)(μ-(+)-tart)]-$(ClO_4)_3$ should have 'Δ' absolute configuration of ligands around vanadium (III) ions.

The CD spectra of oxidized mononuclear species (+)-[$VO(bpy)_2Cl]ClO_4$ and its hydrolyzed product (+)-cis [$VO(bpy)_2OH_2]^{2+}$ ion has a broad negative CD band and may be assigned a 'Λ' absolute configuration. It is likely that an inversion has taken place during oxidation of V(III) into V(IV) and subsequently its conversion into a cis mononuclear species. It is a unique example of stable dissymmetric vanadyl complex which has been achieved through coordinated (+)-tartrate ion in a binuclear species.

CONCLUSIONS

These studies were undertaken to investigate the Pfeiffer effect in new complexes of ligands closely related with 1,10-phenanthroline and 2,2-bipyridyl. A number of Co^{2+}, Ni^{2+} and Cu^{2+} complexes of ligands like 2-aminomethylpyridine, pyridine-2-carboxylic acid and 2,2-bipyridylamine were synthesized and their Pfeiffer effect studies were carried out in presence of chiral environment substances like (+)-α-methylbenzylamine.HCl, (-)cinchonidine.HCl, NH_4-α-BCS, NH_4-10-CS and (+)ascorbic acid. Unfortunately these complexes are very labile and environment substances readily displace these ligands in aqueous systems. Only two complexes $[Co(BPA)_3]^{2+}$ and $[Cu(2\text{-}ampy)_2]^{2+}$ were stable enough to show this effect in presence of NH_4 (+)-α-BCS and NH_4-(-)-10-CS.

The Pfeiffer effect studies in a series of mixed ligand Chromium (III) complexes such as $[Cr(AA)_2X_2]^{n+}$ (where AA = 1,10-phenanthroline or 2,2-bipyridyl and X_2 = anions like Cl^-, oxalate, glycinate or water) were carried out in presence of (+)-cinchonine.HCl, (-)cinchonidine HCl or (+)-tartaric acid. Commonly Chromium (III) is an inert ion and substitution reactions in chromium (III) complexes under room temperature are extremely slow. Optically active complexes like (+)-$[Cr(en)_3]Cl_3$ and (+)-$[Cr(phen)_3]Cl_3$ do not racemize under room temperature conditions. Further a number of such mixed ligands complexes have already been resolved. These complexes also show the Pefiffer effect in presence of (+)-cinchonine HCl, (-)-cinchonidine HCl and (+)-tartaric acid.

The Pfeiffer effect was studied in a series of complexes of poly amine carboxylic acids (e.g. H_4EDTA and H_5DTPA). A number of complexes like$[Cr(EDTA)H_2O]^-$, $[Cr(DTPA)]^{2-}$, $[V(DTPA)]^{2-}$, $[Fe(EDTA)]^-$, $[Fe(DTPA)]^{2-}$,$[Ni(EDTA)]^-$, $[Ni(DTPA)]^{2-}$ $[Nd(EDTA)]^-$,$[Pr(EDTA)]^-$, were investigated. Only $Cr^{3+}$and V^{3+} complexes of these two ligands show the Pfeiffer effect in presence of (+)-cinchonine HCl, (-)-cinchonidine HCl, (+)-tartaric acid, (+)-α-methylbenzylamine HCl, (+) ascorbic acid and (-)-brucine HCl. $[Nd(EDTA)]^-$ shows the Pfeiffer effect in presence of (+)-tartaric acid and (-)-cinchonidine HCl which is dependent upon pH of the system. In basic medium $EDTA^{4-}$ ion is partially replaced by the environment substance. The Pfeiffer effect is induced in a number of complexes in presence of new chiral environment substances such as (-)-cinchonidine HCl (+)-α-methylbenzylamine HCl, (-)-ephedrine HCl, (-)-brucine HCl and (+)-ascorbic acid. It is concluded from these studies that (-)-cinchonidine HCl and (+)-ascorbic acid induced the Pfeiffer effect in many complexes while (-)-ephedrine HCl, (-)-brucine HCl and (-)-quinine HCl induced this effect in only one or two complexes.

CD spectra of these Pfeiffer active systems were measured and Cotton bands were assigned to various electronic transitions after comparing them with their obsorption spectra. In many cases larger number of Cotton band were observed due to splitting of degenerate energy levels in lower symmetry molecules. This is a unique application of CD spectra of the Pfeiffer active complexes. Of course the CD spectra of the Pfeiffer systems may be measured only in visible region (i.e. 450-700 nm) where chiral environment substances have no bands. CD studies in high frequency UV region 450-200 nm cannot be carried out because very strong Cotton bands of the chiral environment substances are commonly present in this region. CD studeies and sign of Pfeiffer effect in these systems have been utilized in ascertaining the absolute configuration of ligands around metal ions. The mixed ligands Cr(III) complexes like cis-$[Cr(AA)_2X_2]^{n+}$ generally show a negative Pfeiffer effect in presence of (+)-cinchonine HCl indicating the enrichment of their *leva* rotatory enantiomers. The CD spectra of these systems when compared with that of $K_3[Cr(ox)_3]$ in presence of (+) cinchonine HCl were found to have Cotton bands of same sign. Therefore *leva* enantiomers of complexes like cis-$[Cr(phen)_2Cl_2]Cl$, cis-$[Cr(bpy)_2Cl_2]Cl$, cis-$[Cr(bpy)_2(H_2O)_2]Cl_3$, $[Cr(bpy)_2gly]Cl_2$ and (+)-$[Cr(phen)_2(ox)]Cl$ have been assigned the same Δ absolute configuration as that of (+)-$K_3[Cr(ox)_3]$. Furhter *dextra* enantiomers of $K[Cr(EDTA)H_2O]$, is assigned Δ absolute configuration.

It is concluded from CD studies of binuclear complexes of V(III) like $[V_2(AA)_4(\mu\text{-}OH)_2]^{4+}$ (AA = phen or bpy) in presence of (+)-tartaric acid that in solution (+)-tartrate ion is coordinated with the metal ion displacing hydroxy bridge, thereby exhibiting strong Cotton bands. The insoluble perchlorate salts of these complexes were readily separated. Redissolution of these complexes as chlorides indicated that Cotton bands intensity was decreased with time and purple V(III) complex was oxidized into a green coloured moiety which could be isolated as $[VO(bipy)_2Cl](ClO_4)$.

The effect of ligand concentration on the CD spectra of aqueous solutions containing binuclear complex and (+)-T.A was studied. Cotton band intensity is linearly increased with increasing i~~n~~ concentration of the ligand indicating that amount of undissociated dissymmetric binuclear complex increases with increasing concentration of the ligand. The solution CD spectra of binuclear complexes $[V_2(AA)_4(\mu\text{-}OH)_2]^{4+}$ in presence of (+)-tartaric acid was thoroughly investigated and sequence of reactions explained. In these systems synthesis of and asymmetric vanadyl complex i.e. (+)-cis-$[VO(AA)_2Cl](ClO_4)$ was achieved.

CD studies of these systems have been utilized to assign Δ absolute configuration around the binuclear species, (+)-$[V_2(phen)_4(\mu\text{-}tart)](ClO_4)_4$ and (+)-$[V_2(bpy)_4(\mu\text{-}OH)\text{-}(\mu\text{-}tart)](ClO_4)_3$ and 'Λ' configuration around (+)-cis$[VO(AA)_2Cl](ClO_4)$ complex.

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