

Circular Dichroism Studies on Some Non-resolvable Mixed Ligand Cobalt(II) Complexes

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Summary: Circular Dichroism (CD) spectra of six mixed ligand complexes such as $[\text{Co}(\text{phen})_2(\text{bpy})]^{2+}$, $[\text{Co}(\text{phen})_2\text{gly}]^+$, $[\text{Co}(\text{phen})_2\text{PyCA}]^+$, $[\text{Co}(\text{bpy})_2(\text{gly})]^+$, $[\text{Co}(\text{bpy})_2(\text{phen})]^{2+}$ and $[\text{Co}(\text{bpy})_2\text{PyCA}]^+$ (where phen = o-phenanthroline, bpy = 2,2' bipyridyl, gly = glycinate, PyCA = pyridine 2-carboxylate ion) in presence of different chiral environment compounds in aqueous media are reported. The CD spectra in presence of (+)-tartaric acid, (+)-malic acid and (+)-ascorbic acid consist of a positive band I between 20,408-20,740 cm^{-1} and a stronger, negative band II between 22,222-23,225 cm^{-1} . A mirror image CD was obtained for these complexes in presence of (-)-tartaric acid and (-)-malic acid. The band I is assigned to electron excitation to $^4\text{A}_2$ and band II to $^4\text{A}_1$ upper states. The dextror enantiomers of all these complexes have been assigned absolute Δ configuration around the metal ion.

Introduction

The Pfeiffer effect has been under investigation since 1931 [1]. It is a change in optical rotation of a solution of chiral compound (hereafter called as environment compound) upon addition of certain racemic metal complexes. Initially the effect was observed in tris complexes of transition metal ions with bidentate ligands such as o-phenanthroline or 2,2'-bipyridyl but later studies showed that EDTA and trioxalato complexes also show this effect [2]. A number of chiral environment compounds such as ammonium (+)-bromocamphorsulphonate, (+)-10-camphorsulphonic acid, (+) or (-) tritaric and malic acids and (+)-cinchonine hydrochloride effectively induce the effect in complexes. In certain cases, it was possible to partially resolve the complex either by precipitation of the complex or environment compound [3,4].

With the development of ORD and CD instruments, newer aspects of this effect were revealed. It was found that ORD spectra of the Pfeiffer systems after making adjustments for rotation of the environment compound are similar to those of resolved enantiomers in tris complexes. Since environment compounds do not absorb in visible region of spectrum, therefore, CD spectra of these systems in this region is mainly due to enrichment of one enantiomer of the complex. Therefore it is not surprising that CD spectra of complexes like $[\text{Co}(\text{ox})_3]^{3-}$ and $[\text{Cr}(\text{ox})_3]^{3-}$ ions in presence of various chiral environment compounds were similar to those of resolved enantiomers [5]. These obser-

vations were later extended to a number of non-resolvable complex ions and CD spectra of $[\text{V}(\text{ox})_3]^{3-}$, $[\text{Fe}(\text{ox})_3]^{3-}$ and $[\text{Co}(\text{phen})_3]^{2+}$ were reported [6]. However CD spectra of mixed ligand complex ions of the type $[\text{M}(\text{AA})_2(\text{BB})]^{n+}$ have never been reported. CD spectral studies of the Pfeiffer effect systems provide a very simple and easy method for investigation since majority of these complexes cannot be resolved by laboratory techniques. The CD spectra of Pfeiffer systems provide valuable information about their absolute configuration and splitting of d-d absorption bands due to lower symmetry of such complexes.

We wish to report CD spectra of a number of non-resolvable mixed ligand complexes of type $[\text{Co}(\text{AA})_2(\text{AB})]^{n+}$ (AA - BB are o-phenanthroline, 2,2'bipyridyl and AB are glycine or pyridine-2-carboxylate ions) in presence of chiral environment compounds like (+), and (-) tartaric and malic acids and (+) ascorbic acid.

Experimental

All reagents were of analytical reagent grade and were used without further purification. o-phenanthroline and 2,2'-bipyridyl were obtained from Fluka, A.G. Switzerland and used as such. The complexes $[\text{Co}(\text{phen})_2(\text{bpy})]\text{Cl}_2$ and $[\text{Co}(\text{phen})(\text{bpy})_2]\text{Cl}_2$ were synthesised and characterized by literature method [4] and other com-

plexes as $[\text{Co}(\text{phen})_2\text{gly}]\text{Cl}$, $[\text{Co}(\text{phen})_2\text{PyCA}]\text{Cl}$, $[\text{Co}(\text{bpy})_2\text{gly}]\text{Cl}$ and $[\text{Co}(\text{bpy})_2\text{PyCA}]\text{Cl}$ were prepared by an analogous procedure. All these complexes were prepared by adding calculated amounts of the two ligands separately dissolved in methanol to a well stirred methanol solution of cobalt(II) chloride hexahydrate. The resulting yellow solutions were stirred for 15 minutes, brought to reflux and kept as such for another 30 minutes. The volume of the reaction solution was reduced to half and kept at room temperature for several hours in an open beaker. During this period crystals of the complexes were formed and separated. The products were recrystallized from methanol and dried in air. These compounds were characterized by their metal analyses and absorption spectra. The results are given in Table-1.

Table-1: Metal analysis and absorption spectra of mixed ligand complexes

Complex	Percentage of Cobalt		Absorption Spectra	
	Calcd.	Found	λ_{maxnm}	$\nu_{\text{cm}^{-1}}$
1. $[\text{Co}(\text{phen})_2(\text{bpy})]\text{Cl}_2$	9.12	9.26	488	20,491
2. $[\text{Co}(\text{phen})_2\text{gly}]\text{Cl}$	11.15	11.17	470	21,276
3. $[\text{Co}(\text{phen})_2(\text{PyCA})]\text{Cl}$	10.22	10.06	490	20,408
4. $[\text{Co}(\text{bpy})_2(\text{phen})]\text{Cl}_2$	9.47	9.53	482	20,746
5. $[\text{Co}(\text{bpy})_2\text{gly}]\text{Cl}$	12.26	12.38	472	21,052
6. $[\text{Co}(\text{bpy})_2(\text{PyCA})]\text{Cl}$	11.15	10.61	460	21,739

Solutions

Solutions for spectral observations were prepared as follows:

Stock solutions of chiral environment compounds (0.32 M) were prepared by dissolving calculated amounts in distilled water and diluted to 1000 mL in a volumetric flask. These solutions were thoroughly mixed and kept in dark in a stoppered bottle.

A calculated amount of appropriate complex (0.04 M) was dissolved in a small volume of the stock environment solution, transferred to a 25-ml volumetric flask and diluted to the mark with the same solution. The solutions were thoroughly mixed and kept in dark for 3-4 hours before recording their spectra. The base line of the spectra were recorded using chiral environment stock solution in the cell.

The absorption spectra of these systems were also measured and compared with those of pure complexes in order to check any interaction between the complex and environment compound.

Instrumentation

The CD spectra of these systems were recorded on JASCO - 20A spectropolarimeter. Strain free quartz cells of 10 mm thickness were used for recording these spectra. Concentrations of these complexes were in the range $1-4 \times 10^{-3}$ moles/litre. The molar concentrations of environment compounds were maintained 4-8 times as those of the complexes. The spectra were recorded in varying concentrations of the environment compounds and only representative spectra are reproduced.

The absorption spectra of aqueous solutions ($1-5 \times 10^{-3}\text{M}$) of these complexes were recorded on Hitachi Model 100-50 recording spectrophotometer. A matched pair of quartz cells of 10 mm thickness were used.

The metal contents of these complexes were determined on Shimadzu model 670 AA atomic absorption spectrophotometer. For sample preparation, accurately weighed amounts of the complexes were decomposed with nitric acid, evaporated to dryness. The remaining mass was dissolved in distilled water in a volumetric flask. These solutions were aspirated in the flame of the instrument and absorptions were measured.

Results and Discussion

A number of racemic mixed ligand complexes such as $[\text{Co}(\text{phen})_2(\text{bpy})]^{2+}$, $[\text{Co}(\text{Phen})_2\text{gly}]^+$, $[\text{Co}(\text{phen})_2\text{PyCA}]^+$, $[\text{Co}(\text{bpy})_2(\text{phen})]^{2+}$, $[\text{Co}(\text{bpy})_2\text{gly}]^+$, $[\text{Co}(\text{bpy})_2\text{PyCA}]^+$ were investigated for their Pfeiffer activity. These complexes show a positive Pfeiffer effect in presence of (+) and (-) tartaric acid, (+) and (-) malic acid and (+) ascorbic acid. These systems show CD bands in the visible region of spectrum. The CD band positions alongwith molar ellipticities of these complex ions in presence of different environment substances are given in Table-2 and their spectra are reproduced in Figs. 1-6.

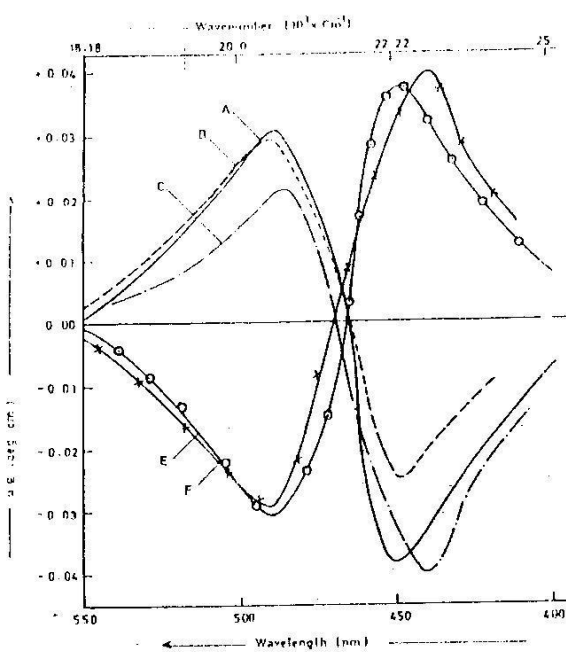


Fig.1: CD spectra of $[\text{Co}(\text{phen})_2(\text{bpy})]^{2+}$ ion in presence of (A). (+)-tartaric acid, B (+)-malic acid, C.(+)-ascorbic acid, E. (-)- malic acid, F. (-)-tartaric acid.

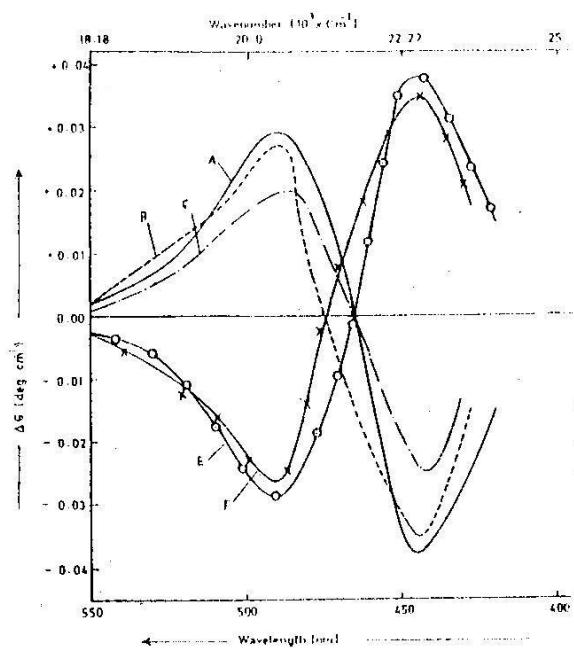


Fig. 2: CD spectra of $[\text{Co}(\text{phen})(\text{bpy})_2]^{2+}$ ion in presence of A (+)-tartaric acid, B.(+)-malic acid, C.(+)-ascorbic acid, E.(-)- malic acid, F.(-)-tartaric acid.

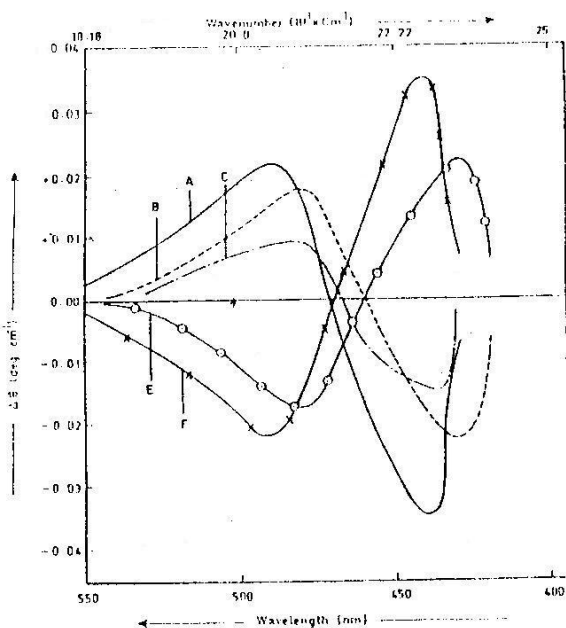


Fig. 3: CD spectra of $[\text{Co}(\text{phen})_2\text{gly}]^+$ ion in presence of A. (+)-malic acid, B.(+)-tartaric acid C.(+)-ascorbic acid, E.(-)- tartaric acid, F.(-)-malic acid.

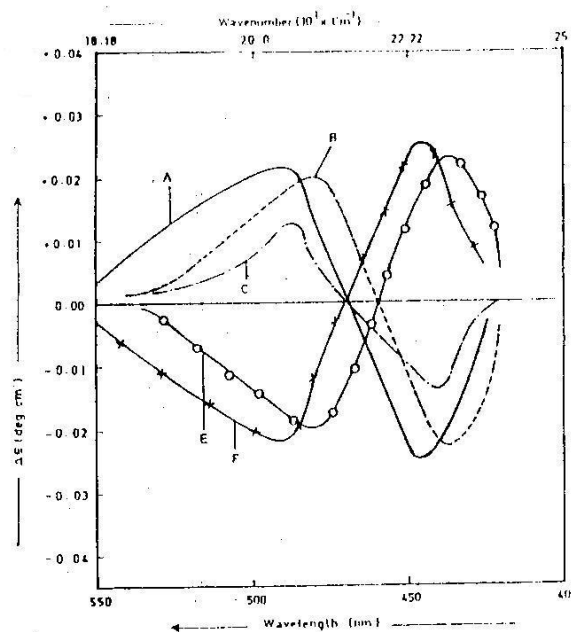


Fig.4: CD spectra of $[\text{Co}(\text{phen})_2\text{PyCA}]^+$ ion in presence of A. (+)- malic acid, B. (+)-tartaric acid, C.(+)-ascorbic acid, E.(-)- tartaric acid and F.(-)-malic acid.

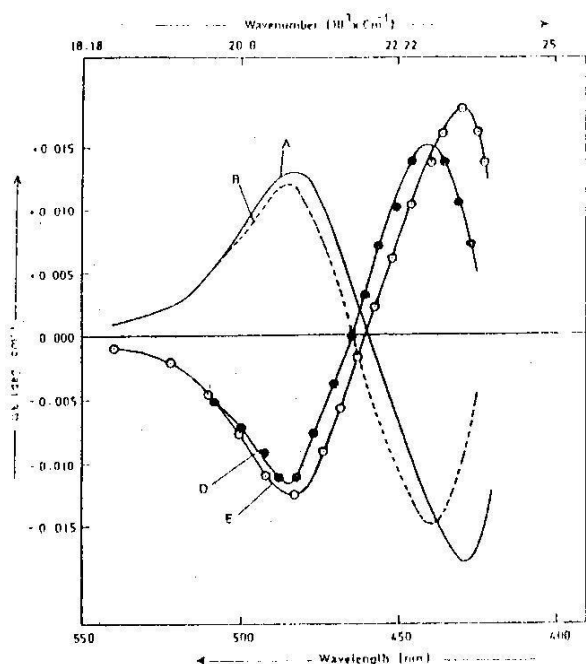


Fig. 5: CD spectra of $[\text{Co}(\text{bpy})_2\text{PyCA}]^+$ ion in presence of A. (+)- tartaric acid, B. (+)-malic acid, D. (-)-malic acid, and E. (-)- tartaric acid.

The chiral environment compounds do not absorb in visible part of the spectrum. Therefore, it is conveniently assumed that CD bands in these systems are due to metal complexes. It is observed that CD of these mixed ligand complexes in presence of (+) tartaric acid, (+) malic acid and (+) ascorbic acid invariably consist of two bands of opposite sign (positive Cotton band on longer wavelength side). The position of these bands do not change in presence of these chiral environment compounds. Since these systems show a positive Pfeiffer effect (i.e., optical rotation of the system is enhanced upon addition of racemic complex), this group of CD spectra is due to *dextro* enantiomers of the complexes. Further, CD spectra in presence of (-) tartaric acid and (-) malic acid are similar in shape but mirror image of those obtained in presence of *dextro* environment compounds. It may be inferred that the second group of spectra are due to *levo* enantiomers of these complexes.

The CD spectra of these systems consist of two well defined bands in the visible region. The first band of positive sign (Band I) is observed be-

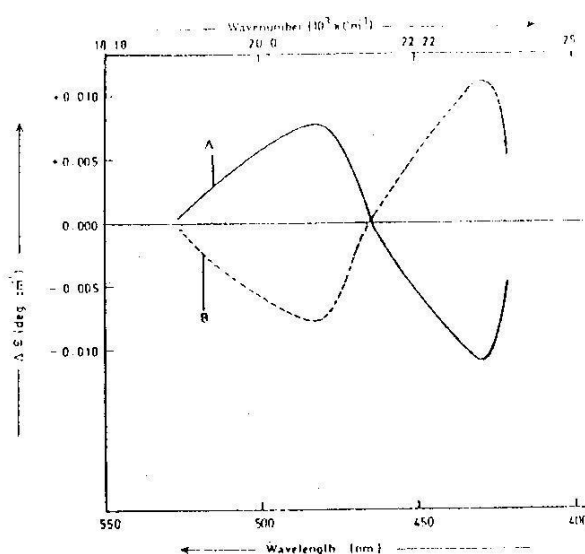


Fig. 6: CD spectra of $[\text{Co}(\text{bpy})_2\text{gly}]^+$ ion in presence of A. (+)- tartaric acid and B. (-)-tartaric acid.

tween 20,408 - 20,746 cm^{-1} while another, stronger negative band (Band II) is found between 22,222 - 23,255 cm^{-1} . The molar ellipticity values of Band I are in the range 0.309 - 2.673 and that of Band II are 0.421 - 3.3 $\text{cm}^{-1} \text{mole}^{-1}$. These ellipticity values increase with increasing concentration of the environment compounds in the system.

The CD studies of a number of Pfeiffer systems containing $[\text{M}(\text{ox})_3]^{3-}$ and (+) cinchonine hydrochloride revealed that their spectra match in every detail with those of pure resolved complexes [5]. Therefore it was concluded that CD spectra of the Pfeiffer systems is a true replica of those of resolved chelates. This technique was later applied to a number of non-resolvable labile complexes [6]. The CD spectra of a few non-resolvable chelates including $[\text{Co}(\text{phen})_3]^{2+}$ in presence of various chiral compounds has already been reported [6]. The three CD bands observed for $[\text{Co}(\text{phen})_3]^{2+}$ ion (two weaker bands of positive sign and a high frequency, stronger band of negative sign) have been assigned to various electronic transitions. The spectra of present series of mixed ligand complexes are comparable to that of $[\text{Co}(\text{phen})_3]^{2+}$ ion with the exception that very weak band centered at 18,690 cm^{-1} for the later was found absent in these systems.

Table-2: CD spectra and molar ellipticity values of mixed ligand cobalt(II) complexes (0.04 M) in presence of chiral environment compounds (0.32 M)

Complex	Environment Compound	Band I (cm ⁻¹)	B ₁ → ⁴ A ₂ (⁴ T _{1g} (P)) [θ] ₁ ml mol ⁻¹ × 10 ⁻³	BAND II (cm ⁻¹)	⁴ B ₁ → ⁴ A ₁ (⁴ T _{1g} (P)) [θ] ₁ ml mol ⁻¹ × 10 ⁻³
[Co(phen) ₂ (bpy)]Cl ₂	(+)-TA	+20,408	2673	-22,222	3300
	(+)-MA	+20,408	2475	-22,424	3300
	(+)-AA	+20,491	1856	-22,222	2475
	(-)-TA	-20,408	2673	+22,222	3300
	(-)-MA	-20,408	2475	+22,242	3300
[Co(phen) ₂ gly]Cl	(+)-TA	+20,576	1443	-23,201	1856
	(+)-MA	+20,408	1856	-22,624	2887
	(+)-AA	+20,618	717	-22,935	1237
	(-)-TA	-20,576	1443	+23,201	1856
	(-)-MA	-20,408	1856	+22,624	2887
[Co(phen) ₂ (PyCA)]Cl	(+)-TA	+20,491	1560	-22,321	1856
	(+)-MA	+20,408	1815	-22,471	2062
	(+)-AA	+20,325	717	-22,727	1130
	(-)-TA	-20,491	1560	+22,321	1856
	(-)-MA	-20,408	1815	+22,471	2062
[Co(bpy) ₂ (phen)]Cl ₂	(+)-TA	-20,408	2392	-22,471	3093
	(+)-MA	+20,408	2268	-22,421	2887
	(+)-AA	+20,491	1650	-22,522	2062
	(-)-TA	-20,408	2392	+22,471	3093
	(-)-MA	-20,408	2268	+22,421	2887
[Co(bpy) ₂ (PyCA)]Cl	(+)-TA	+20,703	1113	-23,255	1303
	(+)-MA	+20,618	990	-22,831	1237
	(-)-TA	-20,703	1113	+23,255	1303
	(-)-MA	-20,618	990	+22,831	1237
[Co(bpy) ₂ (gly)]Cl	(+)-TA	+20,746	309	-23,255	453
	(-)-TA	-20,746	309	+23,255	453

TA = Tartaric Acid, MA = Malic Acid, AA = Ascorbic acid gly = glycinate ion PYCA = pyridine-2-carboxylate ion.

The cobalt(II), d⁷ system, has a triply degenerate ⁴T_{1g} ground state in perfectly octahedral complexes. The d-d spectra of octahedral Co(II) complexes are expected to show three spin allowed absorption bands. A number of six coordinated complexes of this metal ion have been investigated and show two bands which have been assigned to ν₁ and ν₃ electronic transitions to ⁴T_{2g} and ⁴T_{1g}(P) upper levels. The tris complexes [Co(phen)₃]Cl₂ or [Co(bpy)₃]Cl₂ and their mixed ligand analogues such as [Co(phen)₂(bpy)]Cl₂ or [Co(phen)₂gly]Cl being of low symmetry belong to D₃, C₂ or C₁ groups. In such systems, degeneracy of various levels of Oh is lifted to give one dimensional levels. As splitting of degenerate levels is of small order, absorption spectra usually consist of broad bands as evidenced in case of [Co(bpy)₃]²⁺ ion which shows ν₁ 11,260 and ν₃ 16,000 cm⁻¹. However, room temperature crystal spectrum of this ion consists of two bands at 22,000 cm⁻¹ and 18,500 cm⁻¹. The band at 22,000 cm⁻¹ has been assigned to spin allowed ⁴T_{1g}(P) upper level [7].

The CD technique is more sensitive and electronic transitions occur in such a manner that either left handed or right handed circularly polarized light is absorbed to larger extent resulting in positive or negative Cotton bands. As such, broad absorption bands due to several closely situated transitions may decompose to give a number of CD bands of opposite sign. In such cases, CD bands may be assigned to excitation of electrons to various levels in low symmetry species with greater certainty.

The absorption spectra of these mixed ligand complexes consist of only one band between 20,408 - 21,739 cm⁻¹ due to excitation to ⁴T_{1g}(P) upper state in an approximate Oh field. However due to lower symmetry of these complexes, the degenerate levels no longer exist and three one dimensional (A_g, B_g) levels are formed, of which two are expected to be dichroic. The transition to ⁴A₂(Oh) upper level will also be dichroic in these lower symmetry complexes.

The two CD bands observed in these systems have comparable intensity, (Band II is slightly more intense than Band I) and have opposite sign of Cotton effect. It seems that both bands arise from spin allowed transitions to upper states. The ground state in these systems belong to 4B_1 component of ${}^4T_{1g}$ level of Oh molecules. The lower energy Band I may be assigned to 4A_2 while higher energy band II to 4A_1 components of ${}^4T_{1g}$ (P) upper state. This is consistent with the assignment in that $B_1 \rightarrow B_1$ transitions are magnetically forbidden. These assignments correspond closely with those already reported for the crystals spectra of $[Co(bpy)_3]Br_2 \cdot 6H_2O$ and CD spectra of $Co(L-histidine)_2 \cdot H_2O$, $Co(II)$ -carboxylate complexes [8,9].

Certain useful conclusions about absolute configuration of ligands around the metal ion can be drawn from these studies. The CD spectra of these complexes in presence of (+) tartaric acid, (+) malic acid and (+) ascorbic acid is similar to that (+)- $[Co(phen)_3]Cl_2$. It may be concluded that (+)- $[Co(phen)_2(bpy)]Cl_2$, (+)- $[Co(phen)_2gly]Cl$, (+)- $[Co(phen)_2PyCA]Cl_2$, (+)- $[Co(bpy)_2(phen)]Cl_2$, (+)- $[Co(bpy)_2gly]Cl$ and (+)- $[Co(bpy)_2PyCA]Cl$ all have Δ configuration of ligands around the metal ion similar to that of Δ - $[Co(phen)_3]Cl_2$. The *levo* rotatory enantiomers of these complexes enriched in presence of (-)-tartaric acid and (-)-malic acid, have mirror image spectra and should have the same absolute configuration as Δ - $[Co(phen)_3]Cl_2$ i.e., around the metal ion.

The CD bands in presence of (+) ascorbic acid in some of these complexes are slightly shifted towards higher energy. This shifting may be due to some association of the chiral compound with the ligands. This association is particularly prominent in the band II region where bands due to environment start appearing. The nature of this association phenomenon is unknown. Further studies are in progress for ascertaining the nature of this association.

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