

Circular Dichroism Studies of Some Pfeiffer Active Mixed Ligand Chromium(III) Complexes

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Summary: Circular Dichroism (CD) spectra of a series of mixed ligand complex ions such as $\text{cis-[Cr(phen)}_2\text{Cl}_2]^+$, $\text{[Cr(phen)}_2\text{ox}]^+$, $\text{cis-[Cr(bpy)}_2\text{Cl}_2]^+$, $\text{[Cr(bpy)}_2\text{gly}]^{2+}$ and $\text{cis-[Cr(bpy)}_2\text{(H}_2\text{O)}_2]^{3+}$, (phen 1,10 phenanthroline, bpy 2,2'- bipyridyl, gly glycinate and ox oxalate ion) in presence of (+)-cinchonine HCl, (-)-cinchonidine HCl and (+)-tartaric acid have been studied. The CD spectra of these complexes in presence of (+)-cinchonine HCl and (+)-tartaric acid consist of two Cotton bands of opposite sign. The lower energy negative band I is observed between $16,667\text{-}16,949\text{ cm}^{-1}$ ($[\theta]$ $0.5\text{-}11.9\text{ deg. l. mole}^{-1}\text{ cm}^{-1}$). The higher energy positive band II is observed between $19,607\text{-}20,000\text{ cm}^{-1}$ ($[\theta]$ $1.25\text{-}10.0\text{ deg. l. mole}^{-1}\text{ cm}^{-1}$). These complexes have a mirror image spectra in presence of (-)-cinchonidine HCl. These CD bands have been assigned to electronic excitation to A_1 and B_2 upper states. The levo rotatory enantiomers of these complexes except $\text{[Cr(phen)}_2\text{ox}]^+$ enriched in presence of (+)-cinchonine HCl, have been assigned Δ absolute configuration around the metal ion. The levo rotatory enantiomer of $\text{[Cr(phen)}_2\text{ox}]^+$ ion is enriched by (+)-cinchonine HCl and has Δ absolute configuration.

Introduction

Circular dichroism studies of the Pfeiffer effect systems composed of racemic metal complexes and chiral environment compounds have been utilized for determining electronic transitions and absolute configuration of ligands around metal ions [1-4]. We have already reported CD spectra of some non-resolvable cobalt(II) complexes and a number of mixed ligand nickel(II) complexes in presence of chiral environment substances [5,6]. The Pfeiffer effect in dissymmetric chromium(III) complexes has not been investigated to an appreciable extent. To date, only one chromium(III) complex, $\text{K}_3\text{[Cr(ox)}_3\text{]}$ has been reported to show the Pfeiffer effect in presence of (+)-cinchonine HCl. This is because of the inert nature of chromium(III) ion. CD studies of a number of stable chromium(III) complexes such as $\text{[Cr(en)}_3\text{]Cl}_3$, $\text{K}_3\text{[Cr(ox)}_3\text{]}$ have been carried out after their resolution [8]. However, it is possible to record CD spectra of racemic complexes of this ion without resolving them through the Pfeiffer effect. The Pfeiffer effect is of great importance in CD studies of dissymmetric complexes.

In perfectly octahedral environment, chromium(III) (d^3 ion) complexes have $^4A_{2g}$ as ground state and three triply degenerate excited states as $^4T_{2g}$, $^4T_{1g}$ and $^4T_{1g}$ (P) to which electrons

may be excited. The absorption spectra of six coordinated complexes of this ion usually consist of a number of bands ranging between $15,770\text{ - }20,960\text{ cm}^{-1}$, $20,820\text{-}25,000\text{ cm}^{-1}$ and $32,400\text{-}37,700\text{ cm}^{-1}$ which have been assigned to ν_1, ν_2 and ν_3 spin allowed transitions respectively [9]. In low symmetry complexes of this ion, triply degenerate levels further split to give non-degenerate states. As a result, a larger number of absorption bands are expected for complexes like $\text{cis/trans[Cr(en)}_2\text{Cl}_2]$ Cl or $\text{K[Cr(EDTA)(H}_2\text{C)]}$. Electronic transitions to split energy levels in low symmetry species cannot be ascertained from absorption spectra due to broadening of bands. However, CD spectra which is a more sensitive technique, may be fruitfully used to investigate electronic excitations to split levels in such complexes.

We wish to report CD spectra of a number of mixed ligand chromium(III) complexes of the type $\text{[Cr(AA)}_2\text{X}_2]^+$ and $\text{[Cr(AA)}_2\text{BB}]^{n+}$ where AA 1,10-phenanthroline or 2,2'-bipyridyl, X Cl^- or H_2O and BB oxalate or glycinate ions) in presence of (+)-cinchonine HCl, (-)-cinchonidine HCl or (+)-tartaric acid as environment substances. The CD bands have been interpreted in terms of electron excitations to non-degenerate levels in these low symmetry complexes. The absolute configuration

around the metal ion has also been correlated with complexes studied earlier.

Results and Discussion

The complex ions, $[\text{Cr}(\text{phen})_2\text{Cl}_2]^+$, $[\text{Cr}(\text{bpy})_2\text{Cl}_2]^+$, $[\text{Cr}(\text{phen})_2\text{ox}]^+$, $[\text{Cr}(\text{bpy})_2\text{gly}]^{2+}$ and $[\text{Cr}(\text{bpy})_2(\text{H}_2\text{O})_2]^{3+}$ all show a negative Pfeiffer effect at 589 nm in presence of (+)-cinchonine HCl and (-)-cinchonidine HCl. The molar Pfeiffer rotations of these complexes are relatively very small compared to those of earlier studied complexes like $\text{K}_3[\text{Cr}(\text{ox})_3]$. It seems that levo rotatory enantiomers of these complexes are enriched in presence of (+)-cinchonine HCl while dextro enantiomers are enriched in presence of (-)-cinchonidine HCl. The optical rotation of (+)-tartaric acid in presence of $[\text{Cr}(\text{bpy})_2\text{Cl}_2]^+$ or $[\text{Cr}(\text{bpy})_2\text{gly}]^{2+}$ was slightly increased, indicating a weak positive Pfeiffer effect. However, CD spectra of these complexes in presence of (+)-tartaric acid are similar to those obtained in presence of (+)-cinchonine HCl indicating that both of these environment substances enrich the same enantiomers of these complexes.

The absorption spectra of these complex ions consist of single bands between 18,867, -20,202 cm^{-1} with extinction coefficients 62-112 $\text{M}^{-1}\text{cm}^{-1}$. This band may be assigned to spin allowed transition ${}^4\text{A}_{2g} \longrightarrow {}^4\text{T}_{2g}(\nu_1)$.

The CD spectra of these complexes in presence of (+)-cin.HCl is a mirror image of those observed in presence of (-)-cind.HCl. The CD spectra of these complexes (except that of $[\text{Cr}(\text{phen})_2\text{ox}]^+$) in presence of (+)-cin.HCl and (+)-tartaric acid consist of two oppositely signed Cotton bands (Fig. 1-3), a negative low energy band I between 16,667 - 16,949 cm^{-1} with molar ellipticity 0.5- 11.9 deg. 1. mole $^{-1}$ cm^{-1} and a positive band II between 19,607 - 20,000 cm^{-1} ($[\theta]$ 1.25-10.0 deg. 1. kole $^{-1}\text{cm}^{-1}$). The CD spectrum of $[\text{Cr}(\text{phen})_2\text{ox}]^+$ ion in presence of (+)-cin.HCl (Fig. 4) consists of only one negative Cotton band at 20,000 cm^{-1} ($[\theta]$ 1.25-1.87 deg.1.mole $^{-1}\text{cm}^{-1}$). Since (+)-cin.HCl enriches levo enantiomers of these complexes, it may be assumed that observed Cotton bands in these systems are due to levo enantiomers while those observed in presence of (-)-cind.HCl are due to dextro enantiomers of these complexes.

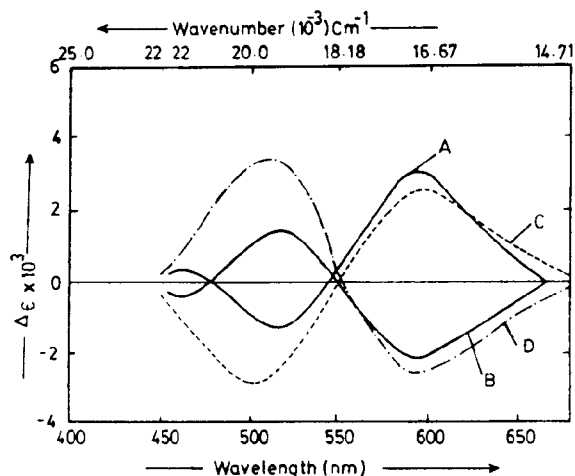


Fig. 1: CD spectra of aqueous solution of $[\text{Cr}(\text{phen})_2\text{Cl}_2]^+$ ion (0.025M) in presence of 0.15 M environment (A) (-)-Cinchonidine HCl, (B) (+)-Cinchonine HCl, and CD spectra of aqueous solution of $[\text{Cr}(\text{bpy})_2(\text{H}_2\text{O})_2]^{3+}$ (0.04M) in presence of 0.12M environment (C) (-)-Cinchonidine HCl and (D) (+)-Cinchonine HCl.

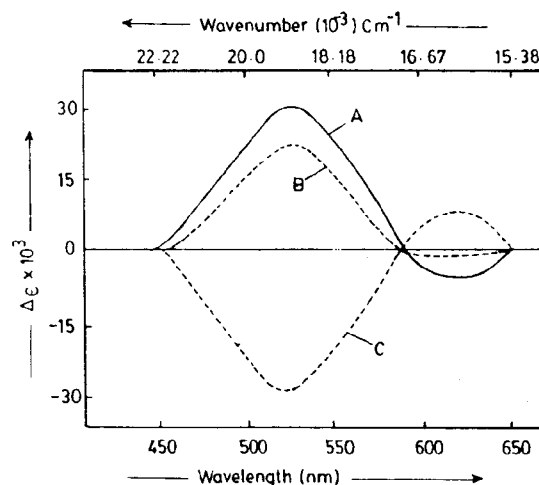


Fig. 2: CD spectra of aqueous solution of $[\text{Cr}(\text{bpy})_2\text{Cl}_2]^+$ ion (0.025 M) in presence of (A) (+)-Cinchonine HCl (0.075M) (B). (+)-Tartaric Acid (0.1M) and (C). (-)-Cinchonidine HCl (0.075M).

Octahedral complexes of chromium (III) being d^3 system have a ${}^1\text{A}_{2g}$ as ground state and three triply degenerate higher energy quartet states as ${}^4\text{T}_{1g}$, ${}^4\text{T}_{2g}$ and ${}^4\text{T}_{1g}(\text{P})$. Excitations of electrons to these levels give rise to three bands due to spin allowed transitions ν_1 , ν_2 , ν_3 . However, in lower

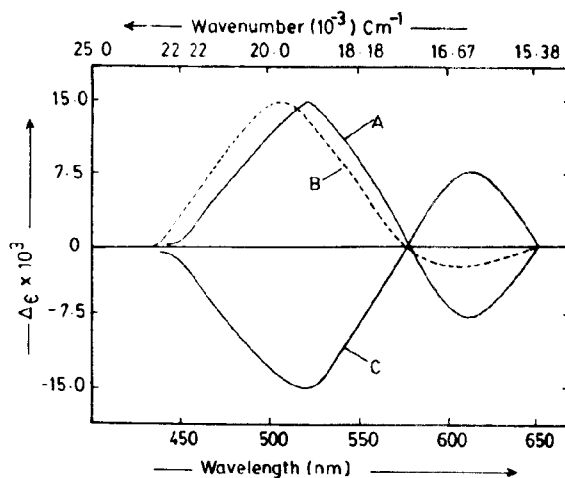


Fig. 3: CD spectra of aqueous solution of $[\text{Cr}(\text{bpy})_2\text{gly}]^{2+}$ ion (0.025 M) in presence of 0.025 M environment (A) (-)-Cinchonidine HCl (B) (+)-Tartaric Acid and (C) (-)-Cinchonidine HCl.

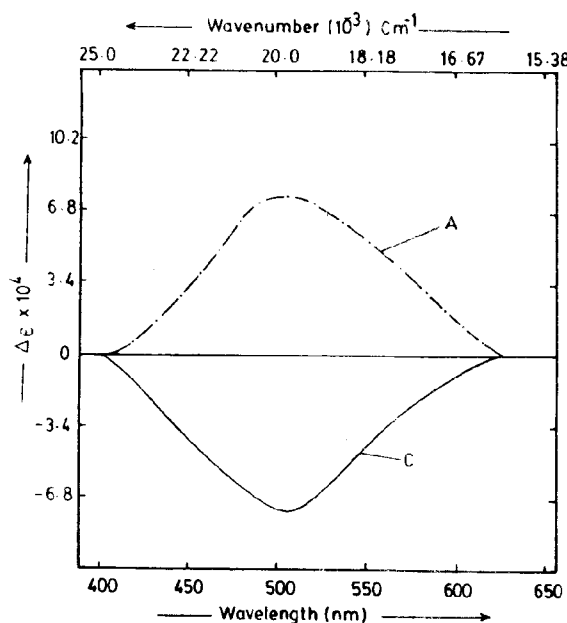


Fig. 4: CD spectra of aqueous solution of $[\text{Cr}(\text{bpy})_2\text{ox}]^{2+}$ ion (0.02 M) in presence of 0.08 M environment (A) (-)-Cinchonidine HCl, (C) (+)-Cinchonine HCl.

symmetry octahedral complexes degenerate levels further split to give one dimensional levels. The present series of complexes belong to C_2 or C_1 point groups. In this symmetry, ${}^4T_{1g}$ or ${}^4T_{2g}$ states split to give 4A_1 , 4A_2 and 4B_2 levels. The positions of absorption and CD band II of these complexes

are comparable. The absorption band due to ν_1 is quite broad in these complexes. The two Cotton bands I and II in these complexes are observed within ν_1 region indicating that these bands arise from excitation of electrons to split levels of ${}^4T_{1g}$ state. Therefore band I in these systems may be assigned to excitation of electrons to A_1 upper level while band II arise from excitation to B_2 upper state. The single Cotton band at $20,000\text{ cm}^{-1}$ in the spectrum of $[\text{Cr}(\text{phen})_2\text{ox}]^+$ ion may be assigned to $A_2 \rightarrow B_2$ transition.

It is possible to correlate the absolute configuration of present series of complexes with those of standard compounds. The complexes (-)-D-cis- $[\text{Cr}(\text{phen})_2\text{Cl}_2]\text{Cl}$, (-)-D-cis- $[\text{Cr}(\text{bpy})_2\text{Cl}_2]\text{Cl}$, (-)-D-cis- $[\text{Cr}(\text{bpy})_2(\text{H}_2\text{O})_2]\text{Cl}_3$ and (-)-D- $[\text{Cr}(\text{bpy})_2\text{gly}]\text{Cl}_2$ should have the same absolute configuration around the metal ions as that of (+)-D- $\text{K}_3[\text{Cr}(\text{ox})_3]$ or (-)-D- $\text{K}_3[\text{Co}(\text{ox})_3]$ since all of these enantiomers are enriched in presence of (+)-cinchonine HCl. The complexes (+)-D- $\text{K}_3[\text{Cr}(\text{ox})_3]$, (-)-D- $\text{K}_3[\text{Co}(\text{ox})_3]$ and (+)-D- $[\text{Co}(\text{en})_3]\text{Cl}_3$ all have been assigned Δ configuration around the metal ions. Therefore levo enantiomers of cis- $[\text{Cr}(\text{phen})_2\text{Cl}_2]\text{Cl}$, cis- $[\text{Cr}(\text{bpy})_2\text{Cl}_2]\text{Cl}$, cis- $[\text{Cr}(\text{bpy})_2(\text{H}_2\text{O})_2]\text{Cl}_3$, $0.5\text{H}_2\text{O}$ and $[\text{Cr}(\text{bpy})_2\text{gly}]\text{Cl}_2$ may be assigned Δ absolute configuration around the metal ion.

The CD spectrum of $[\text{Cr}(\text{phen})_2\text{ox}]^+$ ion in presence of (+)-cinchonine HCl consists of a negative Cotton band which resembles with band II of the other complexes observed in presence of (-)-cinchonidine HCl. Therefore, (-)-D- $[\text{Cr}(\text{phen})_2\text{ox}]\text{Cl}$ may be assigned Λ absolute configuration around the metal ion.

Experimental

All the reagents and solvents used were of highest purity, analytical reagent grade and used without further purification. The ligand 2,2'-bipyridyl, 1,10-phenanthroline and glycine were obtained from Fluka, Switzerland.

The complexes $[\text{Cr}(\text{bpy})_2\text{Cl}_2]\text{Cl}$, $[\text{Cr}(\text{phen})_2\text{Cl}_2]\text{Cl}$ and $[\text{Cr}(\text{phen})_2\text{ox}]\text{Cl}$ were synthesised by already reported methods [10,11]. These complexes were characterized by their metal analyses and absorption spectra. Two new mixed ligand complexes as $[\text{Cr}(\text{bpy})_2\text{gly}]\text{Cl}_2$ and $[\text{Cr}(\text{bpy})_2(\text{H}_2\text{O})_2]\text{Cl}_3 \cdot 0.5\text{H}_2\text{O}$ were prepared by a similar method as given below:

Table 1: Physical data, metal analysis and absorption spectra of mixed ligand complexes of chromium (III).

Complex	Colour	Decomp. temp. °C	% of chromium		Absorption spectra (cm ⁻¹) (ε M ⁻¹ cm ⁻¹)
			Calcd.	Found.	
1. [Cr(phen) ₂ Cl ₂]Cl.3H ₂ O	Orange red	145	9.08	8.80	19,029 (77)
2. [Cr(bpy) ₂ Cl ₂]Cl.2H ₂ O	Bright red	200	10.25	10.0	19,146 (42)
3. [Cr(bpy) ₂ (H ₂ O) ₂]Cl ₃ .0.5H ₂ O	Greyish red	170	10.08	10.20	18,867 (64)
4. [Cr(bpy) ₂ gly]Cl ₂	Bright red	180	10.21	9.80	19,230 (112)
5. [Cr(phen) ₂ ox]Cl.4H ₂ O	Orange red	230	8.55	8.10	20,202 (62)

Table 2: CD band positions and molar Pfeiffer rotations of mixed ligand complexes in presence of chiral environment substances in water solutions

Complex (conc.)	Environment substance (conc.)	Molar Pfeiffer rotation [P _M]D ^o	CD BANDS		BAND II ν _{cm⁻¹}	[θ] deg.l.mole ⁻¹
			BAND I ν _{cm⁻¹}	[θ] deg ₁ l.mole ⁻¹		
1. [Cr(phen)Cl ₂] ⁺ (0.025M)	(+)-Cinch.HCl (0.15 M)	-400	16,806	-8.0	19,607	+6.00
	(-)-Cinchd.HCl (0.15M)	-400	16,806	+11.9	19,607	-5.0
2. [Cr(bpy) ₂ Cl ₂] ⁺ (0.025 M)	(+)-Cinch.HCl (0.075 M)	-800	16,667	-2.5	19,230	+10.0
	(-)-Cinchd.HCl (0.075 M)	-800	16,667	+2.5	19,230	-10.0
	(+)-T.A (0.1 M)	+240	16,667	-0.50	19,230	+7.00
3. [Cr(bpy) ₂ (H ₂ O) ₂] ³⁺ (0.04M)	(+)-Cinch.HCl (0.12M)	-400	16,949	-6.25	19,607	+8.25
	(-)-Cinchd.HCl (0.12 M)	-400	16,949	+6.25	19,607	-7.00
4. [Cr(bpy) ₂ gly] ²⁺ (0.025M)	(+)-Cinch.HCl (0.2 M)	-1200	16,667	-2.00	19,230	+5.00
	(-)-Cinchd.HCl (0.20M)	-1200	16,667	+2.00	19,230	-5.00
	(+)-T.A (0.1M)	+1875	16,667	-0.50	20,000	+5.00
5. [Cr(phen) ₂ ox] ⁺ (0.02 M)	(+)-Cinch.HCl (0.08 M)	-240			20,000	-1.25
	(-)-Cinchd. HCl (0.08 M)	-260			20,000	+1.60

Cinch (+)-cinchonine HCl, Cinchd. HCl Cinchonidine HCl, T.A. Tartaric Acid

Hydrated chromic chloride CrCl₃.6H₂O (2.66 g, 0.01 mole) was dissolved with stirring in 50 ml of methanol in a flask fitted with reflux condenser. A piece of mossy zinc (thoroughly washed with dil. HCl and then water) was placed in metal ion solution. The solution was slowly brought to reflux. Then a solution containing 3.14 (0.02 mole) of 2,2'

bipyridyl in 10 ml methanol was added followed by another solution containing 0.01 mole of glycine or pyridine 2-carboxylic acid in water, to the metal ion solution. The reaction mixture was refluxed for 2 hours. During refluxing, colour of the reaction solution was changed to reddish brown. The solution was concentrated on a water bath to a small volume

and kept at room temperature for 12 hours, during which crystals were formed. The product was filtered, washed with methanol followed by ether and dried in air. Anal. Calculated for $[\text{Cr}(\text{C}_{10}\text{H}_8\text{N}_2)_2\text{C}_2\text{H}_4\text{NO}_2]\text{Cl}_2$ C 51.88, H 3.96, N 13.75% Found. C 52.13, H 3.82, N 12.83%. Calculated for $[\text{Cr}(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_2]\text{Cl}_3 \cdot 0.5\text{H}_2\text{O}$ C 46.57, H 4.10, N 10.86, Cl 20.6%. Found C 46.46, H 3.59, N 10.90, Cl 20.10 %.

Solution for the Pfeiffer effect and CD studies

(a) Stock solutions of chiral environment substances such as (+)-cinchonine HCl/cinchonidine HCl (0.2 M) were prepared by suspending accurately weighed amounts of the alkaloids in 50 ml of water and dropwise addition of dilute hydrochloric acid with thoroughly mixing after each addition. The clear solution was diluted to 100 ml in a volumetric flask.

A 0.2 M stock solution of (+)-tartaric acid was prepared by dissolving an accurately weighed amount of the acid in distilled water and diluting to 100 ml in a flask.

Accurately weighed amounts of the metal complexes were dissolved in small volume of water (5 ml) and mixed with requisite volume of the stock solution of the environment substance in a 25 ml flask to give a 0.02M metal complex solution. A blank containing only the environment substance was also prepared by diluting the stock solution appropriately. These solutions were kept in dark for 1-2 hours and their optical rotations and CD spectra were measured.

Instrumentation

Elemental analyses were carried out at Micro-analytical Labs., Department of Chemistry, University of Glasgow (U.K). Metal contents of these complexes were determined by atomic absorption method on a Shimadzu model 670 AA spectrophotometer.

The solution spectra of these complexes were measured on a Hitachi model 100-50 spectrophotometer using a matched pair of 10 mm quartz cuvettes. The metal analyses and absorption spectra are given in Table 1.

The CD spectra were recorded on a JASCO model J-20A spectropolarimeter using 1-10 mm quartz cells. The CD spectra of these systems in presence of different chiral environment substances are reproduced in Figure 1-4 and their band positions alongwith molar ellipticity values and molar Pfeiffer rotations are given in Table 2.

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