

Circular Dichroism Studies of Pfeiffer Active Vanadium(III) and Chromium(III) Complexes of Ethylenediaminetetracetate (EDTA⁴⁻) and Diethylenetriaminepentacetate (DTPA⁵⁻) ions

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Summary: The Pfeiffer effect has been investigated in aqueous solution of [Cr(EDTA)H₂O]⁻, [Cr(DTPA)]²⁻, [V(EDTA)]⁻ and [V(DTPA)]²⁻ ions in presence of various chiral environment substances, such as (+)-cinchonine HCl, (-)-cinchonidine HCl, (+)-tartaric acid and (-)-tartaric acid, (+)- α -methylbenzylamine HCl, (+)-ascorbic acid, (-)-brucine HCl and (-)-ephedrine HCl. The CD spectra of these complex ions in presence of different chiral environment substances have been reported and Cotton bands assigned to electronic transitions. From the Pfeiffer effect and CD studies, (+)_D-[Cr(EDTA).H₂O]⁻, (+)_D-[Cr(DTPA)]²⁻, (+)_D-[V(EDTA)]⁻ and (+)_D-[V(DTPA)]²⁻ are assigned Δ absolute configuration around the metal ions.

Introduction

The change in optical rotation of a solution of certain chiral compounds in presence of racemic metal complexes, commonly known as the Pfeiffer effect, has been under investigation for more than half a century. The Pfeiffer effect has been reported in a number of racemic complexes like [M(phen)₃]ⁿ⁺, [M(bipy)₃]ⁿ⁺, [M(ox)₃]³⁻, [M(phen)_x(bipy)_{3-x}]ⁿ⁺ and [Cr(phen)₂X₂]ⁿ⁺ (where M=Co(II), Ni(II), Mn(II), Cu(II), Zn(II), x = 1-2 and X=anion or water) in presence of many chiral environment substances [1-4]. Circular Dichroism studies of a number of Pfeiffer effect systems have been utilized for correlating absolute configuration and ascertaining electronic transitions in complexes [5-8]. The Pfeiffer effect is induced in complexes of a limited number of ligands like 2,2 bipyridyl (bipy), *o*-phenanthroline (phen) or oxalate (ox) while complexes like [M(en)₃]ⁿ⁺ or [M(pn)₃]ⁿ⁺ do not show this effect in presence of any chiral compound [9]. However, Kirschner *et al.*, reported a weak Pfeiffer effect in [Cu(EDTA)]²⁻ in presence of (-)-quinine HBr [10]. To the best of our knowledge CD studies of this system have never been reported. Therefore, we have investigated the

Pfeiffer effect in anionic complexes of polyaminocarboxylate ions such as [M(EDTA)]⁻ and [M(DTPA)]²⁻ in presence of new chiral environment substances.

The Pfeiffer effect in [Cr(EDTA)H₂O]⁻, [Cr(DTPA)]²⁻, [V(EDTA)]⁻ and [V(DTPA)]²⁻ ions in presence of various chiral environment substances are reported. Three new compounds as (+)- α -methylbenzylammonium chloride, (-)-ephedrine HCl and (+)-ascorbic acid have been found to be effective for inducing the effect in these racemic complexes. CD spectra of these Pfeiffer systems were studied and interpreted.

Results and Discussion

The Pfeiffer effect was investigated in aqueous solution of anionic complex ions like [V(EDTA)]⁻, [V(DTPA)]²⁻, [Cr(EDTA).H₂O]⁻, [Cr(DTPA)]²⁻ in presence of various chiral environment substances like (+)-cinchonine HCl (CIN.HCl), (-)-cinchonidine HCl (CIND.HCl), (-)-quinine HCl (QUIN.HCl), (+)-tartaric acid, (-)-

tartaric acid (T.A.), (+)- α -methylbenzylammonium chloride (MBA.HCl), (+)-ascorbic acid (AS.A), (-)-brucine HCl, (BRN.HCl), (-)-histidine (HIS.) and (-)-ephedrine HCl (EPH.HCl). A positive Pfeiffer effect was induced in $[\text{Cr}(\text{EDTA})\cdot\text{H}_2\text{O}]^-$ ion in presence of (+)-CIN.HCl, (+)-T.A., (-)-T.A. and (-)-CIND.HCl, while a negative Pfeiffer effect was observed in presence of (+)-AS.A. indicating that (+)_D- $[\text{Cr}(\text{EDTA})\text{H}_2\text{O}]^-$ ion was enriched in presence of (+)-CIN.HCl and (+)-T.A. and (-)_D- $[\text{Cr}(\text{EDTA})\text{H}_2\text{O}]^-$ was enriched in presence of (-)-CIND.HCl, (-)-T.A. and (+)-AS.A. Similarly a positive Pfeiffer effect was induced in $[\text{Cr}(\text{DTPA})]^{2-}$ ion in presence (+)-T.A. and (+)-MBA.HCl and a negative effect was observed in presence of (+)-AS.A. These observations indicate that *dextro* rotatory enantiomer of $[\text{Cr}(\text{DTPA})]^{2-}$ ion is enriched in presence of (+)-T.A. and (+)-MBA.HCl while *levo* rotatory enantiomer of this complex is enriched in presence of (+)-AS.A.

In case of $[\text{V}(\text{EDTA})]^-$ ion, a positive Pfeiffer effect was induced in presence of (+)-MBA.HCl, (+)-T.A., (-)-T.A. and (-)-EPH. HCl while a negative effect was observed in presence of (-)-CIND. HCl and (-)-BRN.HCl. This indicated that *dextro* rotatory enantiomer of $[\text{V}(\text{EDTA})]^-$ ion is enriched in presence of (-)-CIND.HCl, (+)-MBA.HCl, (-)-BRN.HCl or (+)-T.A. while *levo* rotatory enantiomer of this complex ion is enriched in presence of (-)-EPH.HCl or (-)-T.A. A negative Pfeiffer effect was induced in $[\text{V}(\text{DTPA})]^{2-}$ ion in presence of (-)-CIND.HCl and a positive effect was observed in presence of (+)-MBA.HCl indicating that (+)_D- $[\text{V}(\text{DTPA})]^{2-}$ ion is enriched in presence of both of these environment substances. The molar Pfeiffer rotation of these systems (as given in Table-1) are substantially larger in presence of (+)-CIN.HCl, (-)-CIND.HCl or (-)-BRN.HCl as compared to those observed in presence of (+)-T.A., (-)-T.A., (-)-EPH.HCl or (+)-AS.A.

The CD spectrum of $[\text{Cr}(\text{EDTA})\cdot\text{H}_2\text{O}]^-$ ion in presence of (+)-CIN.HCl and (+)-T.A. consists of a broad positive Cotton band I at $17,857 \text{ cm}^{-1}$ ($[\theta] 9.9 - 20.0 \text{ deg.L.mol}^{-1}\text{cm}^{-1}$) while a mirror image spectrum of this ion is obtained in presence of (-)-CIND.HCl, (-)-T.A. and (+)-AS.A. (Fig.1). Another weaker Cotton band II of opposite sign is observed at $20,408 \text{ cm}^{-1}$ ($[\theta] 4.0 \text{ deg.L.mol}^{-1}\text{cm}^{-1}$) in presence of (+)-CIN.HCl and (-)-CIND.HCl.

These bands remain unaltered in presence of different environment substances. The complex $[\text{Cr}(\text{DTPA})]^{2-}$ ion has a positive Cotton band I at $19,230 \text{ cm}^{-1}$ ($[\theta] 9.9 - 16.0 \text{ deg.L.mol}^{-1}\text{cm}^{-1}$) and a negative band at $23,809 \text{ cm}^{-1}$ ($[\theta] 1.65 - 3.3 \text{ deg.L.mol}^{-1}\text{cm}^{-1}$) in presence of (+)-T.A. and (+)-MBA.HCl while a mirror image spectrum was obtained in presence of (+)-AS.A. (Fig. 2).

Absorption spectra of these chromium (III) complexes consist of two bands at $17,699-18,345 \text{ cm}^{-1}$ ($\epsilon = 200 \text{ L.mol}^{-1}\text{cm}^{-1}$) and $21,975 - 25,310 \text{ cm}^{-1}$ ($\epsilon = 180 \text{ L.mol}^{-1}\text{cm}^{-1}$) which are assigned to ${}^4A_{2g} \rightarrow {}^4T_{2g} (\nu_1)$ and ${}^4A_{2g} \rightarrow {}^4T_{1g} (\nu_2)$ transitions respectively in an octahedral field [11]. A comparison of absorption and CD spectra of the two complex ions reveal that couplet of CD bands are closer to the lower energy ν_1 transition while ν_2 is observed at a much higher energy. Since these ions have lower symmetry, the degenerate levels of Oh symmetry split to unidimensional levels. Therefore, Cotton band I in these systems may be assigned to ${}^4A_2 \rightarrow {}^4A_1$ and oppositely signed band II between $20,408-23,809 \text{ cm}^{-1}$ may be assigned to ${}^4A_2 \rightarrow {}^4B_2$ transition.

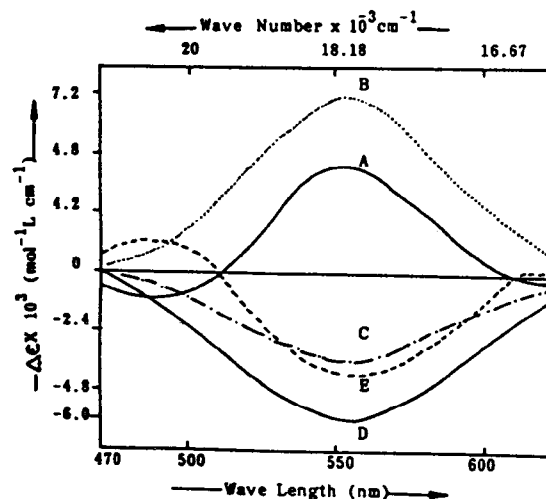


Fig. 1: CD spectra of $[\text{Cr}(\text{EDTA})\text{H}_2\text{O}]^{2-}$ (0.025 mol L^{-1}) in presence of (A). (+)-CIN.HCl (0.1 mol L^{-1}), (B). (+)-T.A. (0.1 mol L^{-1}), (C). (+)-AS.A. (0.1 mol L^{-1}), (D). (-)-T.A. (0.1 mol L^{-1}), and (E). (-)-CIND.HCl (0.1 mol L^{-1}) in aqueous solution.

Table-1: CD and absorption band positions and molar Pfeiffer rotations of the complexes in presence of chiral environment substances in aqueous solution.

Complex (mol L ⁻¹)	Absorption ν cm ⁻¹	Environment Substance (mol L ⁻¹)	Molar Pfeiffer Rotation [PM] _D	Circular Dichroism Bands				
				Band I ν cm ⁻¹	[θ] deg.L. mol ⁻¹ cm ⁻¹	Band II ν cm ⁻¹	[θ] deg.L. mol ⁻¹ cm ⁻¹	Absolute confi-guration of enriched species
1. [Cr(EDTA)H ₂ O] ⁻ (0.025)	15,349 25,641	(+)-CIN.HCl(0.1)	1600.0	17,857	+14.0	20,408	-4.0	Δ
		(-)-CIND.HCl(0.1)	1600.0	17,857	-14.0	20,408	+4.0	Λ
		(+)-T.A. (0.1)	40.0	17,857	+12.0			Δ
		(-)-T.A (0.1)	40.0	17,857	-12.0			Λ
		(+)-AS.A (0.1)	-40.0	17,857	-20.0			Λ
2. [Cr(DTPA)] ²⁻ (0.03)	17,762 24,874	(+)-MBA.HCl (0.12)	40.0	19,230	+16.0	23,809	-1.65	Δ
		(+)-T.A. (0.12)	240.0	19,230	+9.9	23,809	-1.60	Δ
		(+)-AS.A (0.12)	-80.0	19,230	-11.5	23,809	+3.30	Λ
3. [V(EDTA)] ⁻ (0.1)	22,600 19,400(sh)	(-)-CIND.HCl (0.3)	1333.0	19,607	+8.4	23,255	-1.0	Δ
		(+)-MBA.HCl (0.3)	166.7	19,607	+6.4	23,255	-2.0	Δ
		(+)-T.A. (0.3)	200.0	19,607	+2.4	23,255	-1.0	Δ
		(-)-BRU.HCl (0.15)	5333.0	19,607	+4.4	23,255	-1.5	Δ
		(-)-EPH.HCl (0.3)	208.3	19,607	-4.8	23,255	+1.2	Λ
		(-)-T.A. (0.3)	200.0	19,607	-2.4	23,255	+1.0	Λ
4. [V(DTPA)] ²⁻ (0.1)		(-)-CIND.HCl (0.3)	-200.0	16,229	-2.2	21,276	+9.0	Δ
		(+)-MBA.HCl (0.3)	180.6	16,229	-1.2	21,276	+5.0	Δ

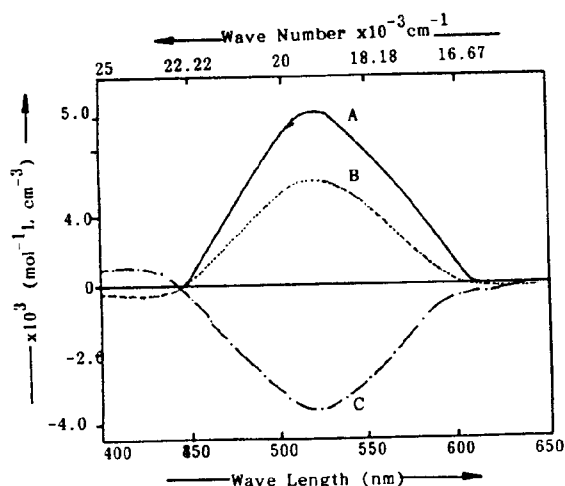


Fig. 2: CD spectra of [Cr(DTPA)]²⁻ (0.03 mol L⁻¹) in presence of (A). (+)-T.A. (0.12 mol L⁻¹), (B). (+)-MBA.HCl (0.12 mol L⁻¹), and (+)-AS.A. (0.12 mol L⁻¹) in aqueous solutions.

The K₃ (+)_D-[Cr(C₂O₄)₃] enantiomer which is enriched in presence of (+)-CIN. HCl, has a major positive Cotton band at 17,986 cm⁻¹ and has been assigned Δ absolute configuration by comparing its CD with standard compounds [7a]. Since (+)_D-[Cr(EDTA).H₂O]⁻ and (+)_D-[Cr(DTPA)]²⁻ enriched in presence of (+)-CIN.HCl or (+)-T.A. show similar Cotton bands (at 17,857 cm⁻¹ and 19,230 cm⁻¹ respectively) they are assigned Δ absolute configuration around the metal ion.

The CD spectrum of [V(EDTA)]⁻ ion (Fig. 3) in presence of (-)-CIND.HCl, (+)-MBA.HCl, (-)-BRN.HCl and (+)-T.A. consists of a positive Cotton band at 19,607 cm⁻¹ ([θ] 2.4-8.4 deg.L.mol⁻¹cm⁻¹) and a negative weaker band II at 23,255 cm⁻¹ ([θ] 1.0-2.0 deg.L.mol⁻¹cm⁻¹) while a

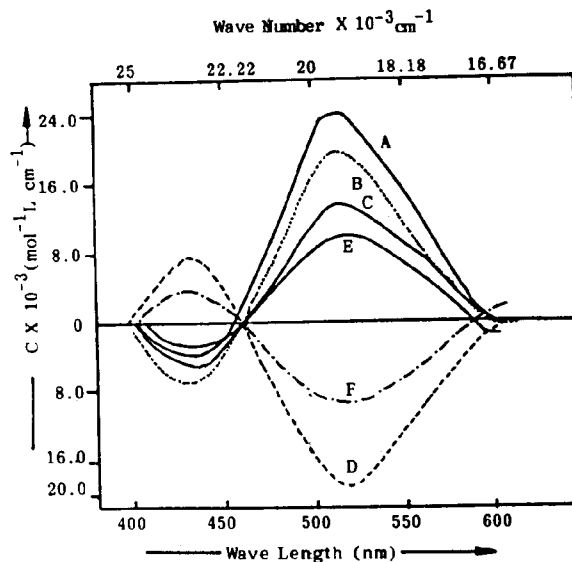


Fig. 3: CD spectra of [V(EDTA)]⁻ (0.1 mol L⁻¹) in presence of (A). (+)-CIND.HCl (0.3 mol L⁻¹), (B). (+)-MBA, HCl (0.3 mol L⁻¹), (C). (-)-BRN HCl (0.3 mol L⁻¹), (D). (-)-EPH.HCl (0.3 mol L⁻¹), (E). (+)-T.A. (0.3 mol L⁻¹) and (F). (-)-T.A. (0.3 mol L⁻¹) in aqueous solution.

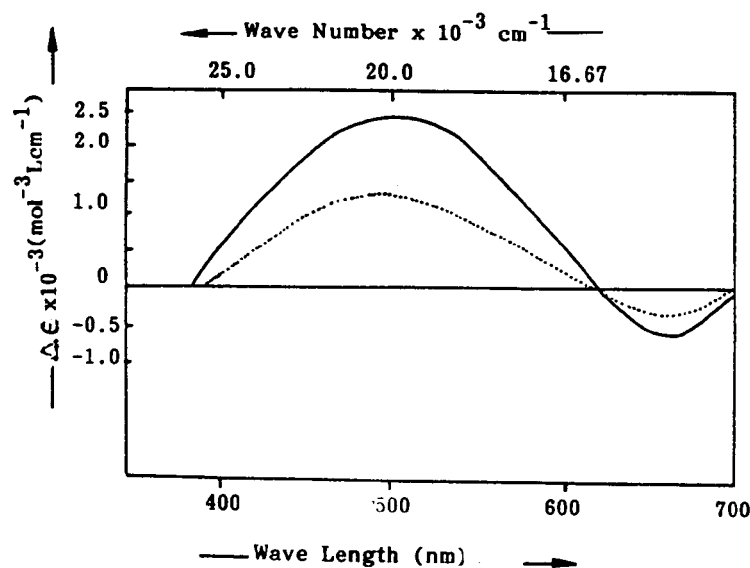


Fig. 4: CD spectra of $[V(DTPA)]^{2-}$ (0.1 mol L^{-1}) in presence of (A). (-)-CIND.HCl (0.3 mol L^{-1}) and (B). (+)-MBA.HCl (0.3 mol L^{-1}) in aqueous solution.

mirror image spectrum was observed in presence of (-)-EPH.HCl and (-)-T.A. Similarly CD spectrum of $[V(DTPA)]^{2-}$ in presence of (-)-CIND.HCl and (+)-MBA.HCl (Fig. 4) consists of a couplet of bands, a lower energy negative band at $16,229 \text{ cm}^{-1}$ ($[\theta]$ $1.2\text{-}2.2 \text{ deg.L.mol}^{-1}\text{cm}^{-1}$) and a stronger positive band at $21,276 \text{ cm}^{-1}$ ($[\theta]$ $5.0 - 9.0 \text{ deg.L.mol}^{-1}\text{cm}^{-1}$). The positive Cotton band between $19,607 - 21,276 \text{ cm}^{-1}$ in these two complexes may be assigned to ${}^3A_1 \rightarrow {}^3A_2$ (${}^3T_{1g}(P)$) transition while band II at $23,255 \text{ cm}^{-1}$ in $[V(EDTA)]$ may be due to excitation of electrons to 3B_1 arising from splitting of ${}^3T_{1g}(P)$ state. The negative Cotton band at $16,229 \text{ cm}^{-1}$ in $[V(DTPA)]^{2-}$ may be due to excitation of electrons to 3B_1 level of ${}^3T_{2g}$ upper state. These band assignments agree with absorption bands reported for a number of octahedral complexes of V(III) ion by other workers [11].

The (+)_D- $[V(EDTA)]^-$ and (+)_D- $[V(DTPA)]^{2-}$ ions are enriched in presence of (-)-CIND.HCl have similar CD spectra. Therefore, these two ions may have same absolute configuration. On the other hand, Λ - $[Cr(EDTA).H_2O]$ is enriched in presence of the same chiral environment substance and has a strong negative Cotton band at $17,857 \text{ cm}^{-1}$. Therefore, (+)_D- $[V(EDTA)]^-$ and (+)_D-

$[V(DTPA)]^{2-}$ ions may be assigned Δ absolute configuration.

From these studies, it is clear that the Pfeiffer effect is induced in vanadium(III) and chromium(III) complexes of $EDTA^{4-}$ and $DTPA^{5-}$ in presence of a number of new chiral environment substances. Further, CD studies of these systems may be used to correlate absolute configuration of these complexes with standard compounds without resolving them into enantiomers.

Experimental

All the reagents, metal salts, ligands, chiral environment substances were of highest purity, analytical reagent grade and were used without further purification. The ligands, Na_4EDTA and H_5DTPA were obtained from Fluka, Switzerland while (+)-cinchonine, (+)- α -methylbenzylamine, (-)-cinchonidine, (+)-ascorbic acid, (+)-tartaric acid and (-)-tartaric acid were purchased from Aldrich (U.S.A.) or BDH, England. Double distilled water was used for preparation of solutions.

The complexes $Na[Cr(EDTA).H_2O]$ and $K_2[Cr(DTPA)].6H_2O$ were prepared using literature methods [12]. Their purity was ascertained from solution absorption spectra.

Na[V(EDTA)] in solution was prepared as reported in literature [13]. Aqueous solution of [V(DTPA)]²⁻ ion was also prepared in an analogous manner by mixing equimolar quantities of VCl₃ and Na₃DTPA in an inert atmosphere. Fresh solutions of V(III) complexes were prepared for each set of experiments to minimize air oxidation.

Solutions for the Pfeiffer effect and CD studies

(a) Stock solutions of chiral compounds such as (+)-cinchonine HCl, (-)-cinchonidine HCl, (-)-brucine HCl, and (+)-methylbenzylammonium chloride (0.2-0.5 mol L⁻¹) were prepared by suspending appropriate amounts of each in 50 ml of water followed by dropwise addition of dilute hydrochloric acid with thorough mixing. The clear solutions were diluted to 100 ml.

(b) Stock solutions of (+) or (-)-tartaric acid, (+)-ascorbic acid and (-)-ephedrine HCl (0.5 mol L⁻¹) were prepared by dissolving appropriate amounts of each in small volume of water and diluting to 100 ml. These solutions were thoroughly mixed and kept in dark.

(c) Accurately weighed amounts of Na[Cr(EDTA)H₂O] (238.3 mg) and Na₂[Cr(DTPA)] (427.0 mg) were dissolved in 5 ml of water and mixed with requisite volume of stock solution of the environment substance in a 25 ml flask to give 0.025-0.030 mol L⁻¹ solution of the complex and 0.1-0.12 mol L⁻¹ with respect to environment compound. These solutions were kept in dark for two hours. Their rotation and CD spectra were recorded.

(d) Appropriate volumes of stock solutions of chiral environment substances were mixed with standard solutions of [V(EDTA)]⁻ or [V(DTPA)]²⁻ and diluted to 25 ml so as to maintain 0.1- 0.12 mol L⁻¹ concentration of the complexes and 0.3 mol L⁻¹ concentration of environment substances.

Instrumentation

Absorption spectra of aqueous solutions of these complexes were measured on a Hitachi model 100-50 spectrophotometer using a matched pair of 10 mm quartz cuvettes. CD spectra were recorded on JASCO model J-20A spectropolarimeter using 1-20 mm quartz cells. Solutions of comparable

concentration of chiral environment substances were used to record baseline of these spectra.

The CD spectra of these systems in presence of different chiral environment substances are reported in Fig. 1-4 and their band positions along with molar ellipticity values and molar Pfeiffer rotations are given in Table-1.

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