Inorganica Chimica Acta, 14 (1975) 215–221

Optical Rotatory Dispersion and Circular Dichroism Spectra of Some Non-resolvable Dissymmetric Metal Complexes

N. AHMAD and S. KIRSCHNER
Department of Chemistry, University of Islamabad, Islamabad, Pakistan
Department of Chemistry, Wayne State University, Detroit, Mich., U.S.A.
Received November 20, 1974

Optical rotatory dispersion and circular dichroism spectra are obtained for certain racemic mixtures of tris complexes of oxalate ion, o-phenanthroline and 2,2′-bipyridyl ligands with metal ions in the presence of optically active organic compounds. These metal complexes have never been resolved (i.e. are non-resolvable by conventional methods) and show the Pfeiffer effect.

The CD spectra of tris(o-phenanthroline)cobalt(II) chloride is obtained in the presence of six different optically active organic compounds and compared amongest themselves. These studies provide strong support for the authenticity of the spectra observed for other similar systems.

The observed CD bands are compared with the absorption bands and assigned to the electronic transitions in certain cases. On the basis of these spectra $(+)_D$-$[Cr(C_2O_4)_3]^{3-}$, $(-)_D$-$[Co(C_2O_4)_3]^{3-}$, $(-)_D$-$[Al(C_2O_4)_3]^{3-}$, $(-)_D$-$[V(C_2O_4)_3]^{3-}$ *and* $(-)_D$-$[Fe(C_2O_4)_3]^{3-}$ *ions are considered to have the same absolute configuration around the metal ions as* $(+)_D$-$[Co(en)_3]^{3+}$ *ion.*

Introduction

Dissymmetric metal complexes can be divided into three groups an the basis of the studies done on their optical activity. i. Optically Inert Complexes: which can be resolved into their optically active enantiomers by experimental means. Their rate of racemization is extremely slow. This group includes the complexes of Co^{3+}, Cr^{3+}, Ru^{3+}, Pt^{4+} ions. ii. Optically Labile Complexes are those which can be resolved into enantiomers, but their rate of racemization is rather fast. The half life of racemization is of the order of few seconds to several hours. This group comprises octahedral complexes of Ni^{2+}, V^{3+}, Fe^{2+} ions. iii. Non-Resolvable Complexes. Although they exist as *levo* and *dextro* enantiomers, they cannot be resolved by the usual experimental methods. The reason for their non-resolvability is considered to be their very high rate of racemization. Commonly tris type complexes of V^{3+}, Fe^{3+}, Co^{2+}, Mn^{2+}, Cu^{2+} ions fall into this category of compounds. Most of the tetrahedral coordination compounds of the type $[M(AB)_2]^{n+}$ (AB is a bidentate ligand having two different donor sites) can also be included in this group.

As the compounds in the first and second groups can easily be isolated into their *dextro* and *levo* rotatory enantiomers, their various aspects especially the spectra (ORD and CD) and absolute configurational studies have created wide interest currently. There is an enormous amount of literature available on this topic which has provided strong support for Werner's theory. On the contrary people have experienced difficulty in studying the coordination compounds of the third group due to their lability and resistance to resolution.

It was found that a few compounds belonging to the three classes show the Pfeiffer effect.[1,2] The Pfeiffer effect is a change (increase or decrease) in the optical rotation of an optically active organic compound present in a solution along with a racemic mixture of a dissymmetric metal complex. The optically active organic molecule will be referred to as "environment substance" hereafter. Recent studies on the nature and mechanism of this effect have produced some fruitful results.[3] Now it is commonly believed that the optical rotation changes observed in these systems are mainly due to production (*in situ*) of a slight excess of one of the optically active enantiomers of the metal complex under the influence of the optically active environment substance present in the system. We have already communicated that partially resolved samples of metal complexes such as $[Ni(phen)_3]^{2+}$ or $[Co(C_2O_4)_3]^{3-}$ can be obtained by removing the metal complex or the optically active organic compound from the Pfeiffer active system.[4] It was also observed that optical rotatory dispersion and circular dichroism spectra of some of the optically inert complexes such as $[Cr(C_2O_4)_3]^{3-}$ and $[Co(C_2O_4)_3]^{3-}$ are exactly similar to those obtained for their Pfeiffer systems without actually resolving them.[5] These observations have an important consequence in that the ORD and CD spectra obtained for the other Pfeiffer systems containing racemic mixture of non-resolvable dissymmetric metal complexes and optically active environment substances should be representative of their *dextro* or *levo* antipodes. This provides a novel method for studying the rotatory dispersion and circular dichroism spectra of optically non-resolvable coordination compounds without making any attempt for their resolution.

In this article we report the ORD and CD spectra of some oxalate complexes which have never been resolved into their optically active enantiomers. Moreover, circular dichroism spectra of *dl*-$[Co(phen)_3]^{2+}$ ion are obtained in the presence of six different optically active environment substances. Different environment substances produce different enantiomers (*D* or *L*) of the metal complex in the Pfeiffer systems. These spectra are exactly similar, except in cases where an opposite enantiomer is produced by the optically active environment substance present in the Pfeiffer system, in which case the spectra are mirror images. This then comfirms that the CD spectra obtained for the non-resolvable complexes are a true representation of those expected for optically pure, *dextro* or *levo* enantiomers of the dissymmetric complex.

Experimental

All the reagents used were of A.R. grade and were used without further purification. $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$, $K_3[V(C_2O_4)_3]\cdot 3H_2O$ and $K_3[Al(C_2O_4)_3]\cdot 3H_2O$ were prepared by the methods reported in the literature.[6,7]

$[Co(phen)_3]Cl_2$ and $[Co(bipy)_3]Cl_2$ were prepared by mixing the methanol solutions of the metal salt and ligand in the molar ratio of 1:3 respectively. The resulting yellow solutions were concentrated on water baths and left overnight. The crystalline complex was separated and dried. Satisfactory elemental analyses were obtained for these compounds. *Anal.* Calculated for $[Co(phen)_3]Cl_2$: C, 64.50, H, 3.58, N, 4.18, Co, 8.8, Cl, 10.58%. Found: C, 64.04, H, 3.7, N, 4.10, Co, 8.71, Cl, 10.70%. Calcd for $[Co(bipy)_3]Cl_2$: C, 60.22, H, 4.01, N, 4.68, Co, 9.85, Cl, 11.86%. Found: C, 59.95, H, 4.30, N, 4.70, Co, 10.10, Cl, 12.01%.

A Cary model 60 spectropolarimeter with CD attachment was used for recording the differential rotatory dispersion and circular dichroism spectra of these systems. A modified sample holder was obtained from the Cary Instruments Co, Monorvia, California, U.S.A., for recording differential rotatory dispersion of the Pfeiffer systems. The sample holder allowed two matched cells to be placed at different positions so that the rotational angle produced by the optically active environment substance and solvent was cancelled. Thus the instrument recorded only the rotatory dispersion curve due to the Pfeiffer effect.

Since the environment substances used in these studies are all organic compounds which do not absorb in the visible region of the spectrum, the circular dichroism spectra of the Pfeiffer active systems in this region were essentially due to the labile metal complexes. Therefore no modification of the CD sample compartment was required.

Absorption spectra in the Vis–NIR region were recorded on a Cary model 14 recording spectrophotometer using 1.0 cm matched cells.

Stock solutions of the optically active environment substances were prepared by carefully dissolving weighed amounts of the solid compounds in water and diluting them to a known volume. A stock solution of *d*-cinchonine hydrochloride was prepared by dropwise addition of a dilute hydrochloric acid solution to a well-stirred slurry of a weighed amount of *d*-cinchonine in water. After dissolution, the solution was stirred for 10 minutes and then diluted in a volumetric flask. Calculated amounts of solid metal complexes were dissolved in aliquot portions of these stock solutions. The samples were left in the dark for 2–3 hours and used for spectral studies. The reference cells were filled with these stock solutions.

The ratio of the molar concentrations of the metal complex to optically active environment compound was 1:2 for bivalent and 1:3 for trivalent complex ions. The molar concentrations of the metal complexes used were of the order $1.0–5.0\times 10^{-2}$, and those of the optically active compound were of the order of $3.0–25.0\times 10^{-2}$.

Results

In a previous communication (*loc. cit.*) we have shown that the Pfeiffer ORD and CD spectra of the systems containing *DL*-$[Cr(C_2O_4)_3]^{3-}$ or *DL*-$[Co(C_2O_4)_3]^{3-}$ and *d*-cinchonine hydrochloride were similar to their resolved, optically pure *dextro* rotatory isomers. In order to substantiate the fact that ORD and CD observed for the Pfeiffer systems are due to the metal complexes, it was considered appropriate to compare the spectra of a non-resolvable metal complex in the presence of a number of different environment substances. Fortunately $[Co(phen)_3]^{2+}$ ion was available which shows this effect in the presence of many optically active substances, such as ammonium *d*-bromocamphor-π-sulphonate, *d*-cinchonine hydrochloride, and *d* and *l* enantiomers of malic and tartaric acids. The CD spectra (shown in Figure 1) of this ion were obtained in the presence of these six environment substances. The main peak positions and their molar ellipticity are produced in Table I.

TABLE I. Circular Dichroism and Molar Pfeiffer Rotations of Systems Containing $[Co(phen)_3]Cl_2$ (0.04*M*) and $[Co(bipy)_3]Cl_2$ (0.05*M*) and Various Environment Substances (0.08*M*).

Environment Substance	Molar Pfeiffer Rotation $[P_M]_D^{23}$ Deg. M^{-2} meter^{-1}	CD Band I[a]		CD Band II[a]		CD Band III[a]	
		λ_{max} (cm^{-1})	$\Delta\varepsilon \times 10^4$	λ_{max} (cm^{-1})	$\Delta\varepsilon \times 10^4$	λ_{max} (cm^{-1})	$\Delta\varepsilon \times 10^4$
NH_4-*d*-BCS[c]	+4078	18,690	+12.5	20,200	+31.78	22,320	− 94.0
d-Malic Acid	+2141	18,690	+12.2	20,200	+38.00	22,320	− 71.0
d-Tartaric Acid	+4127	18,690	+14.5	20,200	+55.50	22,320	−125.0
l-Malic Acid	+2575	18,690	− 8.8	20,200	−32.40	22,320	+ 72.5
l-Tartaric Acid	+4249	18,690	−16.0	20,200	−52.00	22,320	+123.0
d-Cinchonine Hydrochloride	−4000	18,690	−12.0	20,200	−31.70	22,320	+ 91.0
NH_4-*d*-BCS[b, c] (0.25*M*)	+ 604	–	–	–	–	21,740	− 54.3

[a] 5.0 mm cell, 23° C. [b] Values for $[Co(bipy)_3]Cl_2$. [c] Ammonium *d*-Bromocamphor-π-sulphonate.

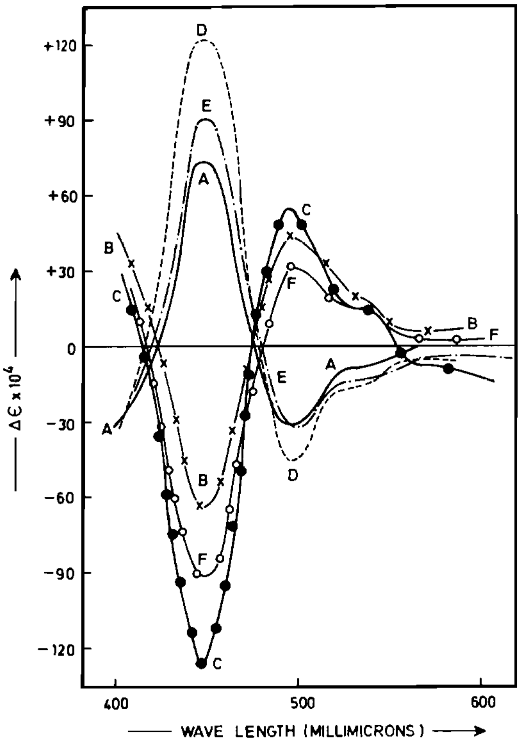

Figure 1. Circular Dichroism spectra of $[Co(phen)_3]Cl_2$ in the presence of (A) *l*-Malic Acid (———), (B) *d*-Malic Acid (—x—x—x—), (C) *d*-Tartaric Acid (—●—●—), (D) *l*-Tartaric Acid (-----), (E) *d*-Cinchonine Hydrochloride (—·—·—), (F) Ammonium *d*-bromocamphor-π-sulphonate (—o—o—).

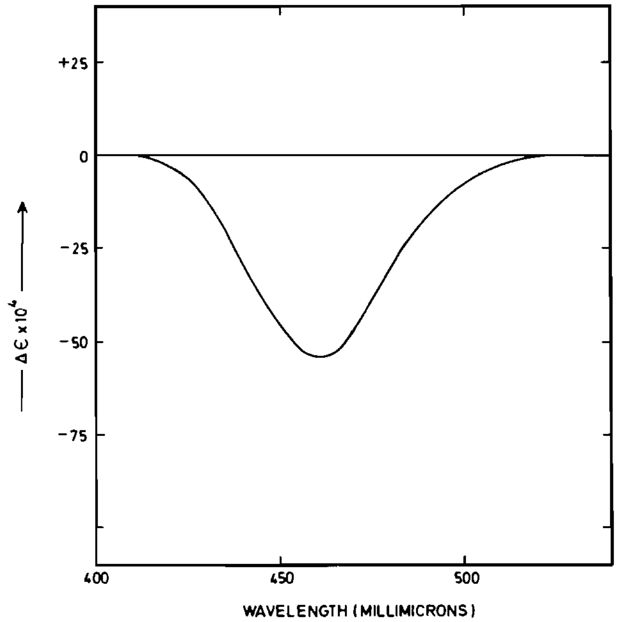

Figure 2. Circular Dichroism spectrum of $[Co(bipy)_3]Cl_2$ in the presence of Ammonium *d*-bromocamphor-π-sulphonate.

It is interesting to note that the CD spectra of $[Co(phen)_3]^{2+}$ ion obtained in the presence of *d*-tartaric acid, *d*-malic acid and ammonium *d*-bromocamphor-π-sulphonate are similar. These spectra only differ in the magnitude of their molar ellipticity. The spectra that are obtained in the presence of *l*-tartaric acid, *l*-malic acid and *d*-cinchonine hydrochloride are also similar except that they are mirror images of the first group of spectra. This indicates that the first group of spectra is due to *dextro* and the second to *levo* antipodes of the complex ions.

$[Co(bipy)_3]^{2+}$ ion also shows the Pfeiffer effect in the presence of optically active organic ions. Unfortunately the changes observed in optical activity of these systems are extremely small and the instrument could not record the weak bands. The CD spectrum obtained for this ion in the presence of ammonium *d*-bromocamphor-π-sulphonate is shown in Figure 2.

Oxalate complexes of the type $K_3[M(C_2O_4)_3]3H_2O$ where M = Al(III), V(III) and Fe(III) are very labile and all efforts for their resolution have failed. The iron(III) complex forms a very stable diastereoisomer with the resolving agent D-$[Co(en)_3]^{3+}$ ion but the isomer remaining in the filtrate showed no optical activity, even when working at lower temperatures near 0° C. The diastereoisomer could not be decomposed for removal of the optically active antipode of the complex ion. The Pfeiffer rotatory dispersion and circular dichroism studies of these ions in the presence of cinchonine hydrochloride were undertaken with a view that Cotton effect bands might be observed. The observed spectra are reproduced in Figures 3 and 4 and data collected in Table II.

$[V(C_2O_4)_3]^{3-}$ ion showed Cotton effect bands both in ORD and CD modes whereas $[Fe(C_2O_4)_3]^{3-}$ ion showed very weak CD bands which overlap with each other. $[Al(C_2O_4)_3]^{3-}$ has a plain curve in the visible region of the ORD spectrum because it has no absorption in this region.

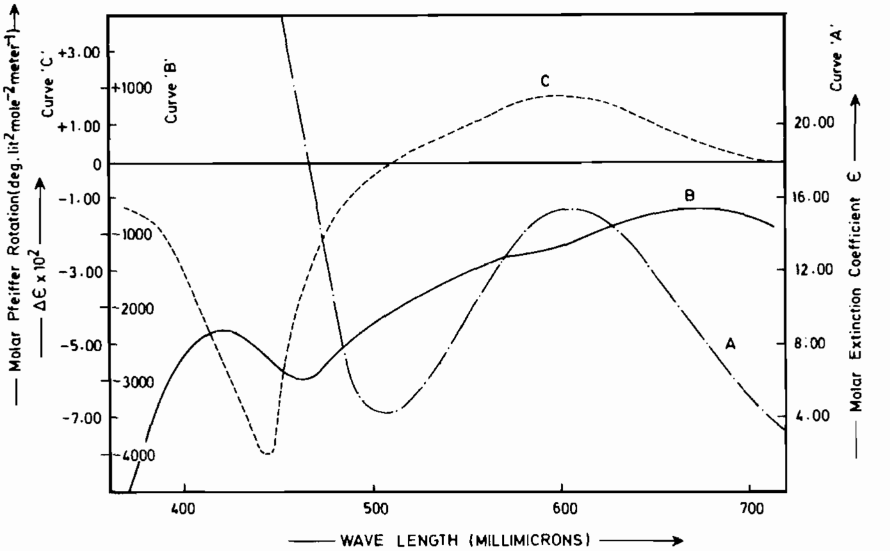

Figure 3. Absorption (—·—·—), Optical Rotatory Dispersion (——) and Circular Dichroism spectra (-----) of $K_3[V(C_2O_4)_3]\cdot 3H_2O$ in the presence of *d*-Cinchonine Hydrochloride.

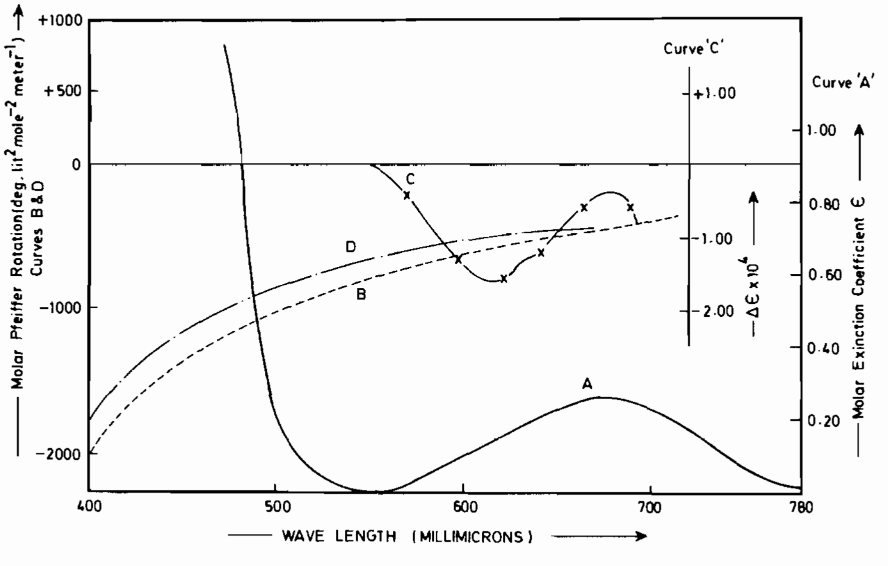

Figure 4. (A) Absorption (——), (B) Rotatory Dispersion (-----) and (C) Circular Dichroism spectra (—x—x—x) of $K_3[Fe(C_2O_4)_3]3H_2O$, (D) Rotatory Dispersion spectrum (—·—·—) of $K_3[Al(C_2O_4)_3]3H_2O$ in the presence of *d*-Cinchonine Hydrochloride.

TABLE II. Pfeiffer Rotations, Absorption and Circular Dichroism Spectra of Non-resolvable Metal Oxalate Complexes.

Complex	Environment Substance	Molar Pfeiffer Rotation $[P_M]_D^{23}$ (deg. M^{-2} meter^{-1})	Absorption	Circular	Dichroism
			λ_{max} (cm^{-1})	λ_{max} (cm^{-1})	$\Delta\varepsilon \times 10^4$
$K_3[Al(C_2O_4)_3]\cdot 3H_2O$	*d*-Cinchonine Hydrochloride	− 534	29,410	–	–
	l-Quinine Sulphate	+3375	29,410	–	–
$K_3[V(C_2O_4)_3]\cdot 3H_2O$	*d*-Cinchonine Hydrochloride	−1533	16,529 22,500(sh)	16,667 22,727	+182.0 −786.2
$K_3[Fe(C_2O_4)_3]\cdot 3H_2O$	*d*-Cinchonine Hydrochloride	− 640	14,925	15,552 16,130	− 1.2 − 1.6

Discussion and Conclusions

Partial resolution of metal complexes through the Pfeiffer effect and similarity of ORD and CD spectra of these systems with those of the resolved enantiomers indicate that the observed spectra in the present investigations are true representations of their optically active antipodes. The CD spectra obtained for $[Co(phen)_3]^{2+}$ ion in the presence of six different optically active compounds is an interesting study. The spectra of *dextro* and *levo* rotatory isomers of the complex are obtained without actually resolving these compounds. The spectra obtained in the presence of *d*-malic acid, *d*-tartaric acid and *d*-bromocamphor-π-sulphonate ion are similar amongst themselves and mirror images of those obtained with *l*-malic acid, *l*-tartaric acid and *d*-cinchonine hydrochloride.

The Pfeiffer effect studies show that the optical rotation of a solution of *d*-cinchonine hydrochloride is appreciably decreased upon the addition of $[Co(phen)_3]^{2+}$ ion in the system. This showed that a slight excess of *levo* enantiomer of the metal complex had been produced in the system. On the other hand, the optical rotations of *levo* rotatory malic and tartaric acids are increased upon the addition of the metal complex, which also indicates the excess of *levo* (–) antipode of the complex in the system. This is confirmed when the CD spectra obtained for the metal complex in the presence of these three environment substances are compared.

The CD spectra of this ion consist of three bands in the visible region. One of these bands lying in the lower wavelength region is the strongest and of the opposite sign to the others. Tris(*o*-phenanthroline)cobalt(II) ion is a high spin d^7 system and has lower symmetry (D_3) than octahedral (O_h). The solution absorption spectra of Co(II) and many other similar ions do not show any splitting of the triplet energy levels because of the lower symmetry.[8,9,10] Therefore the spectra can be explained by effectively approximating to O_h first shell symmetry around the Co(II) complex ions. Thus considering the octahedral crystal field around the metal ion, $^4T_{1g}$ is the ground level. The energy level diagram shows the presence of doublet ($^2T_{1g}$ and $^2T_{1g,2g}$) and quadruplet ($^4T_{1g}$, $^4A_{2g}$) higher states to which the electronic transitions could occur. These higher levels are dichroic as well. Thus the following assignments to the observed bands could be made:

$^4T_{1g} \rightarrow {}^2T_{1g}$ 22.320 cm^{-1}
$^4T_{1g} \rightarrow {}^4T_{1g}(P)$ 20,00 cm^{-1}
$^4T_{1g} \rightarrow {}^2T_{1g,2g}$ 18,690 cm^{-1}

Recently Katzin[11] studied and analyzed the circular dichroism spectra of Co(II) ion in the presence of optically active amino acids. He assumed the formation of 1:1 complex between the metal ion and amino acids. The observed bands in the regions 22,222–20,704, 19,569–18,869, 18,484–16,892 and 16,667–16,000 cm^{-1} were assigned to these electronic transitions by him. Our CD spectra very much resemble that obtained by Katzin and only differ in the lower energy region where one band is not observed.

The CD spectrum of $[Co(bipy)_3]^{2+}$ ion in the presence of ammonium *d*-bromocamphor-π-sulphonate consists of only one negative band with the maximum at 21,735 cm^{-1}. Since ammonium *d*-bromocamphor-π-sulphonate is *dextro* rotatory and its optical rotation is enhanced in the presence of metal complex, *i.e.* an excess of the *dextro* complex is produced in the system, this band should be due to the *dextro* enantiomer of the complex. The strongest band in the CD spectrum of $[Co(phen)_3]^{2+}$ ion in the presence of *d*-bromocamphor-π-sulphonate ion is of the negative sign and situated at 22,320 cm^{-1}. Thus the only band observed in the CD spectrum of $[Co(bipy)_3]^{2+}$ ion can be assigned to the transition $^4T_{1g} \rightarrow {}^2T_{1g}$ of the above mentioned complex. The resolved tris complexes of *o*-phenanthroline and 2,2′-bipyridyl with nickel(II) ion show large differences in their specific rotations (compare $[\alpha]_D^{20} = 1460°$ for *D*-$[Ni(phen)_3]^{2+}$ and 529° for $[Ni(bipy)_3]^{2+}$).[12,13] Similar large differences in Pfeiffer rotations are observed in complexes of Ni (II), Mn(II), Co(II) with the above ligands (compare $[P_M]_D$ for the ions $[Ni(phen)_3]^{2+} = 2696°$, $[Ni(bipy)_3]^{2+} = 484°$, $[Mn(phen)_3]^{2+} = 1850°$, $[Mn(bipy)_3]^{2+} = 525°$ in the presence of *l*-malic acid.[2] Thus it is possible that the ellipticity for the weak bands observed at 18,690 and 20,200 cm^{-1} in $[Co(phen)_3]^{2+}$ ion is decreased to such an extent in $[Co(bipy)_3]^{2+}$ ion that the instrument was unable to record it. Therefore these bands are completely lost in the spectrum of the latter complex ion.

The ORD and CD spectra of $[M(C_2O_4)_3]^{3-}$ ions where M = Al^{3+}, V^{3+} and Fe^{3+} in the presence of cinchonine hydrochloride provide typical results. Aluminum(III) has empty whereas iron(III) has half filled *d* orbitals. Therefore plain ORD spectral curves are expected which are obtained for these complex ions. On the other hand vanadium(III) has two electrons in its *d*-orbitals and on the basis of an energy level diagram (by approximating to O_h first shell symmetry, as stated before), three bands are expected in its absorption, ORD and CD spectra. Commonly only two absorption bands are observed in the visible and near ultraviolet regions of the spectrum. The aqueous solution of $[V(C_2O_4)_3]^{3-}$ ion shows a single band in the visible region centered at 16,529 cm^{-1}. The second band can be obtained at 23,500 cm^{-1} as a shoulder at the tail of strong charge transfer bands in the ultraviolet region. The differential ORD of this complex ions in the presence of cinchonine hydrochloride is unsymmetrical in the region 16,667–14,286 cm^{-1} and shows a Cotton effect band in the 25,000 cm^{-1} region. This clearly indicates two electronic transitions in the visible part of the spectrum.

The CD spectral studies have produced better results and two well defined CD bands are observed with maxima at 16,667 and 22,727 cm^{-1}. The band at 16,667 cm^{-1} is broad, weak and of positive sign whereas the second band is a strong one and of opposite sign. Considering the energy level diagram for a d^2 system in an approximate O_h symmetry, it is possible to assign the electronic transitions $^3T_{1g} \rightarrow {}^3T_{2g}$ for the band at 16,667 cm^{-1} and $^3T_{1g} \rightarrow {}^3T_{1g}(P)$ for the band at 22,727 cm^{-1}. The absorption spectra of $[V(C_2O_4)_3]^{3-}$ ion in aqueous solution was studied by Hartmann and coworkers.[12] These workers assigned the observed bands at 16,450 cm^{-1} to $^3T_{2g}(F)$ and 23,500 cm^{-1} (shoulder) to $^3A_{2g}$ upper states. Later studies[9] of the polarised absorption spectra of crystals of this ion embedded in crystals of $NaMgAl(C_2O_4)_3 \cdot 9H_2O$ have shown that the assignment of the band at 23,500 cm^{-1} was not correct and should be assigned to $^3T_{1g}(P)$ upper state. The circular dichroism bands fit very well into the previously observed absorption spectra of this ion in solution.

The absorption spectrum of an aqueous solution of $[Fe(C_2O_4)_3]^{3-}$ ion has a very weak and broad band which is spread over the region 17,544–12,500 cm^{-1} with the maximum at 14,925 cm^{-1}. A high spin iron (III) in an octahedral crystal field has $^6A_{1g}$ as its ground state and has no higher term with a similar multiplicity. Therefore all the electronic transitions in this ion will be forbidden resulting in a number of very weak and sharp bands. However, a weak broad band may be considered as a resultant of a number of bands overlapping one another. This is apparent from the CD spectrum of this ion in the presence of cinchonine hydrochloride. At least two overlapped and very weak bands at 15,552 and 16,130 cm^{-1} are observed and the trend of the curve is indicative of more bands in the near infrared region which could not be studied. It seems quite difficult to assign these bands to any of the electronic transitions.

From these and earlier studies on the Pfeiffer effect it is possible to correlate the absolute configuration of these metal complexes with those compounds whose structure and absolute configurations are ascertained through other means (such as X-rays diffraction). Thus, considering the sign of the Pfeiffer effect at sodium D line and circular dichroism spectra of these systems, the $(+)_D$-$[Cr(C_2O_4)_3]^{3-}$, $(-)_D$-$[Co(C_2O_4)_3]^{3-}$, $(-)_D$-$[Fe(C_2O_4)_3]^{3-}$, $(-)_D$-$[V(C_2O_4)_3]^{3-}$ and $(-)_D$-$[Al(C_2O_4)_3]^{3-}$ ions should have the same absolute configuration around the metal ion. The absolute configuration of $(-)_D$-$[Co(C_2O_4)_3]^{3-}$ ion has already been correlated to $(+)_D$-$[Cr(C_2O_4)_3]^{3-}$ ion on the basis of their ORD and CD spectra.[13] Further the $(-)_D$-$[Co(C_2O_4)_3]^{3-}$ ion has been assigned the same absolute configuration as that of $(+)_D$-$[Co(en)_3]^{3+}$ ion using a similar technique.[13]

Thus these investigations show that the ORD and CD spectra of nonresolvable dissymmetric complexes can be obtained through the Pfeiffer effect without actually resolving the complex. This further eliminates the chances of quick racemization observed in certain optically labile metal complexes where it becomes very difficult to obtain accurate spectra.

Acknowledgement

The authors gratefully acknowledge the financial support provided by the National Science Foundation, and a graduate fellowship provided by Wayne State University, Detroit, Mich., U.S.A.

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