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The Pfeiffer CD Activity of *d–d* Electronic Excitations of ($Co^{III}S_6$) and ($Cr^{III}S_6$) Chromophores and of [$Co(acac)_3$]

J. D. GUNTER and A. F. SCHREINER
North Carolina State University, Department of Chemistry, Raleigh, 27607, U.S.A.
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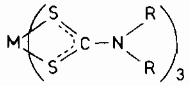
Six molecular complexes of the tris chelate type containing the ($Co^{III}S_6$) and ($Cr^{III}S_6$) chromophores (dithiocarbamate, dithiophosphate, and dithioxanthate ligands) were found to have Pfeiffer CD activity (PCD). Three combinations of environment compounds and solvents were found to induce such optical activity in d–d excitations. However, the PCD effect could only be observed under conditions of using very large concentration ratios of optically active environmental compound to the complex racemate. The PCD bands of magnetically allowed parents, ${}^4T_{2g}$(Cr) and ${}^1T_{1g}$(Co), are found to be most intense. Furthermore, it is established that the trigonal components ${}^4E$(Cr) and ${}^1E$(Co) have much greater intensity than ${}^4A_1$(Cr) and ${}^1A_2$(Co), respectively. It is also found that the empirical model which has previously been used with success to relate absolute configurations of ionic complexes to the chirality of the environment compound leads to ambiguous conclusions when the attempt is made to study (neutral) molecular complexes in this manner.

Introduction

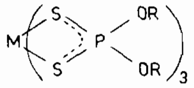
A number of research groups have devoted extensive efforts to relating the absolute configurations of metal complexes to the signs of CD or ORD activities of resolved enantiomers.[1] However, there are only a few laboratories which have explored the question of whether there is a potential of using the Pfeiffer effect for relating the sign of this Pfeiffer CD (or ORD) activity to the absolute configuration of a complex ion.[2] The answer to this question has thus far been affirmative for ionic complexes. For example, one approach[3] which has been explored and used with success for tris complexes, $[M(AA)_3]^{Q+}$, where AA is restricted to *o*-phenanthroline or bipyridine, is based on the dual principles of the exciton computational results[4] and on the center of gravity principle of Hawkins[1b]. In this exciton model the optically active electronic excitations (a) must originate to first order within the D_3 symmetric π system of the coordinated *o*-phen or bipy, (b) the metal–ligand and ligand–ligand interactions (or at least effects on the π system) are assumed to be small perturbations, and (c) the symmetries (${}^1E$ or ${}^1A_2$) of the $\pi \rightarrow \pi^*$ transitions, which originate from the basis orbitals having long-axis polarization of the ligands, ought to be known. The last feature can be determined from the center of gravity of the band system[1b], since ${}^1A_2$ is more intense than ${}^1E$.

The second and more empirical approach which has been explored is founded on the assumption, and substantiated for several complexes, that any one optically active environment compound of a chirality will always produce an excess of one of the two possible, Δ or Λ ($P(C_3)$ or $M(C_3)$), isomers of the complex. Once the specific environment compound is tested with a racemic mixture of which the absolute configuration of one enantiomer is known, then one would study other complexes and establish their absolute configurations on the basis of the signs of ORD or CD bands. This second method has been employed with success for studying ionic complex compounds.[5] This empirical method does not necessitate that the ligands be restricted to any one type. It is implied by this second model that, if one has available a complex which (a) can be dissolved in the Pfeiffer solvent–environment and (b) will have PCD activity, and (c) for which the absolute configuration of one enantiomer has been established, then one application of measuring PCD dispersions is that the latter offers the opportunity of relating the signs of optically active excitations to unknown absolute configurations for any other racemates and other chromophores displaying PCD activity in the same environment.

There is a paucity of Pfeiffer effect data for (neutral) molecular complexes, $[M(AA)_3]^0$, *i.e.,* neither of the above methods has been explored as a possible tool for relating Pfeiffer effect CD data to the absolute configuration of such tris chelate molecules. We were especially interested in compounds containing metal–sulfur bonds,[6] and in this report we communicate our Pfeiffer CD findings for such molecular complexes of these types, tris dithiocarbamato,

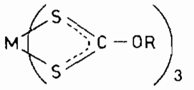


tris dithiophosphato,



and

tris dithioxanthato,



containing cobalt(III) and chromium(III), and for [Co(acac)$_3$]. It was necessary to find new conditions and environment–solvent systems in order to induce the Pfeiffer effect for these molecular species. These findings, the Pfeiffer CD spectra, and the structural implications are reported here.

Experimental Section

Commercially available ligands were complexed with Cr(III) and Co(III) according to the general procedure outlined in the literature.[7] The solutions for the Pfeiffer CD studies were made by dissolving the racemic complex in a small aliquot of the pure solvent, which was followed by diluting with a stock solution composed of the environment compound in the solvent of choice. This dilution of the environment concentration in the stock solution was taken into account in the calculation of Pfeiffer molar ellipticities, $[\Theta]_M{}^P$. All spectra reported were recorded right after the optimal development of optical activity. CD spectra were obtained on a Durrum JASCO ORD/UV/CD-5 spectropolarimeter with the SS-20 modification, which allows the measurement of g-values to 10^{-6}, and electronic absorption spectra were determined on a Cary 14 spectrophotometer and the JASCO. The rate of the development of maximum Pfeiffer CD activity was followed on an external strip chart recorder at the wavelength of a band maximum. The strip chart recorder was interfaced with the JASCO through a modification which was originally designed to output an analog signal of the spectrum to a time averaging computer.

Pfeiffer molar ellipticity, $[\Theta]_M{}^P$, was calculated using the expression

$$[\Theta]_M{}^P = \frac{\alpha}{M_e M_c l}$$

where α = degrees ellipticity observed, M_e = molar concentration of the environment compound, M_c = molar concentration of the metal complex, and l = path length in cm. The units of $[\Theta]_M{}^P$ are degree-liters^2-(mol environment)$^{-1}$-(mol solute)$^{-1}$-cm^{-1}, therefore. Solvent and environmental compounds are specified in the tables and figure captions.

Results and Discussion

All initial attempts carried out in the *d*-camphor–chloroform system failed to produce the Pfeiffer effect for these molecular complexes containing the ($M^{III}S_6$) chromophore, since we kept the concentration of the environment compound low but in the range previously employed. Soon thereafter it was discovered, however, that much higher concentrations than ever used before will induce the effect. Care was taken to keep the optical densities of solutions low so as to prevent distortions of CD band-shapes. Table I shows the conditions under which the Pfeiffer effect was observed. Table II contains the Pfeiffer molar ellipticity values, $[\Theta]_M{}^P$ (*vide supra*), and other numerical data for the six complexes in the three environment systems, *d*-camphor in $HCCl_3$, L-(–)-malic acid in DMSO, and *d*-tartaric acid in DMSO. The band shapes of several of these spectra can be seen in Figures 1–3. These data and spectra are discussed next, and their structural implications are presented below. The nature of these electronic excitations whose Pfeiffer activities are measured are also discussed immediately below.

d-Camphor in Chloroform

The Pfeiffer CD and electronic absorption spectra of three ($Cr^{III}S_6$) complexes of dithiocarbamate,

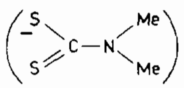


TABLE I. Ratios of Molar Environment Concentration (M_e) to Complex Concentration (M_c) in Three Environments.

	d-Camphor/HCCl$_3$			L-(–)-Malic Acid/DMSO			*d*-Tartaric Acid/DMSO		
Compound	M_e	M_c	M_e/M_c	M_e	M_c	M_e/M_c	M_e	M_c	M_e/M_c
Cr(dmtc)$_3$	2.702	7.120×10^{-3}	379	2.70	5.514×10^{-3}	490	3.0	4.366×10^{-3}	687
Cr(detp)$_3$	2.702	2.546×10^{-3}	1061	2.70	4.357×10^{-3}	620	3.0	2.968×10^{-3}	1011
Cr(exan)$_3$	2.702	5.902×10^{-3}	458	2.70	4.523×10^{-3}	597	3.0	6.154×10^{-3}	487
Co(detc)$_3$	2.702	4.149×10^{-3}	651	2.40	3.823×10^{-3}	628			
Co(detp)$_3$	2.702	3.894×10^{-3}	694	2.70	3.828×10^{-3}	705	3.0	3.427×10^{-3}	875

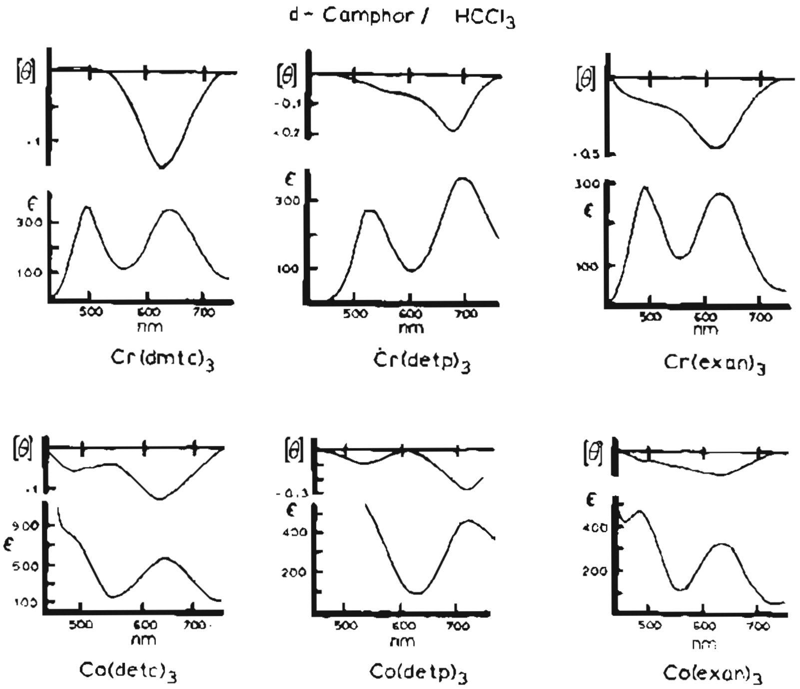
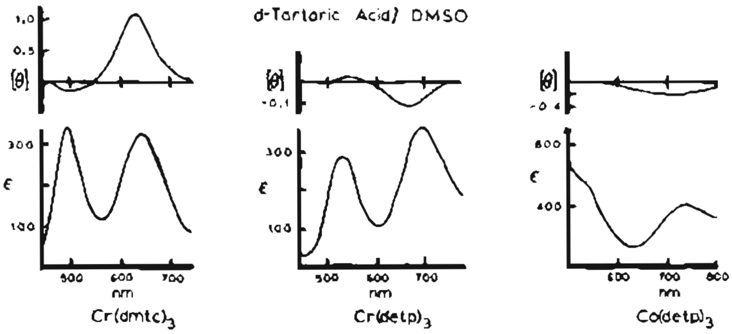

d- Camphor / HCCl$_3$

Figure 1. Electronic Absorption and Pfeiffer CD Spectra in *d*-Camphor/HCCl$_3$.


d-Tartaric Acid/ DMSO

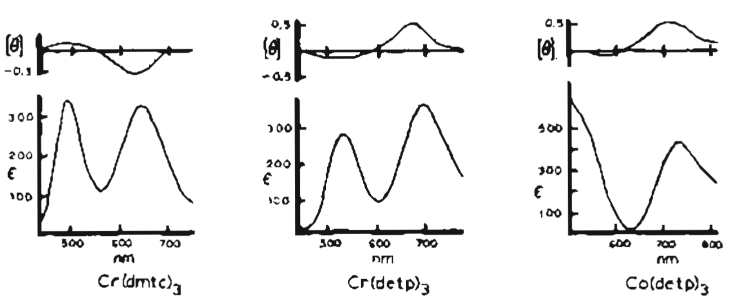
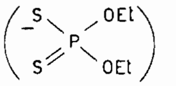
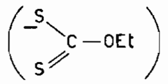

L-(-) Malic Acid / DMSO

Figure 2. Electronic Absorption and Pfeiffer CD Spectra of Several (M^{III}S$_6$) Molecules in *d*-Tartaric Acid/DMSO and L-(–)-Malic Acid/DMSO.

TABLE II. Electronic Absorption and Pfeiffer CD Parameters for ($M^{III}S_6$) Complexes in Various Environments.

Compound	$HCCl_3$		d-Camphor/$HCCl_3$				L-(–)-Malic Acid/DMSO				d-Tartaric Acid/DMSO			
	λ_{max} (nm)	ε_{max}	$[\Theta]$	ε	λ_{CD} (nm)	λ_{ABS} (nm)	$[\Theta]$	ε	λ_{CD} (nm)	λ_{ABS} (nm)	$[\Theta]$	ε	λ_{CD} (nm)	λ_{ABS} (nm)
$Cr(dmtc)_3$	637	331	–1.390	331	624	638	–0.316	328	630	640	1.076	344	630	640
$Cr(detp)_3$	697	369	–0.349	365	678	696	0.502	368	672	695	–0.112	361	690	696
$Cr(exan)_3$	623	289	–0.476	290	620	622	0.0	276	–	622	0.390	300	616	624
$Co(detc)_3$	642	515	–1.285	517	640	643	0.0	536	–	645	–	–	–	–
$Co(detp)_3$	738	445	–0.285	422	720	737	0.542	421	710	739	–0.214	408	720	738

or dmtc$^-$, dithiophosphate,  or detp$^-$, and dithioxanthate,  or exan$^-$, and of the three ($Co^{III}S_6$) analogs are shown in Figure 1. Each spectrum is composed of metal-localized *d–d* bands of type $t_2^6 \rightarrow t_2^5e^1(Co^{III}S_6)$ or $t_2^3 \rightarrow t_2^2e^1(Cr^{III}S_6)$. The states in O_h and D_3 symmetries are as follows:

($Co^{III}S_6$)		($Cr^{III}S_6$)	
O_h	D_3	O_h	D_3
$^1T_{2g}$	^1E	$^4T_{1g}$	^4E
$^1T_{1g}$	$^1E > {}^1A_2$	$^4T_{2g}$	$^4E > {}^4A_1$
($^1T_{2g} > {}^1T_{1g}$)		($^4T_{1g} > {}^4T_{2g}$)	

Only the statically electric and magnetic dipole allowed excited states are given for the symmetry D_3, and the ground states are $^1A_1$(Co) and $^4A_2$(Cr). The polarizations of several of these spin-allowed D_3 bands were established previously[8] for Cr(III) and Co(III) dithiocarbamates and dithiophosphates and the spin-forbidden bands are too weak to be observed.[9] For both series of complexes Figure 1 (also Figures 2 and 3) show that the lowest energy states $^1T_{1g}$(Co) and $^4T_{2g}$(Cr) have the most intense rotational strengths. This is expected on the grounds that these are the magnetically allowed O_h parent states. Furthermore, the net activity of each of these $^1T_1$ and $^4T_2$ bands is negative. Having the same signs for Co(III) and Cr (III) analogs parallels the behavior of natural CD spectra of, for example, resolved $[Cren_3]^{3+}$ and $[Coen_3]^{3+}$ containing the ($M^{III}N_6$) chromomore of *d–d* excitations.[10]

On the basis of the empirical model relating the Pfeiffer activity to absolute configuration as outlined above, each excess enantiomer in these *d*-camphor/$HCCl_3$ solutions would have the same configuration, Λ. This Λ configurational preference of this specific solvent system was established as follows. First, (±)-$[Co(acac)_3]$ was found to be soluble in this solvent system. It was found here that $(-)_{546}$-$[Co(acac)_3]$ is the favored isomer in *d*-camphor/$HCCl_3$. Second, since Fay's new x-ray method[11] established that this enantiomer has the Λ configuration, this structure–Pfeiffer

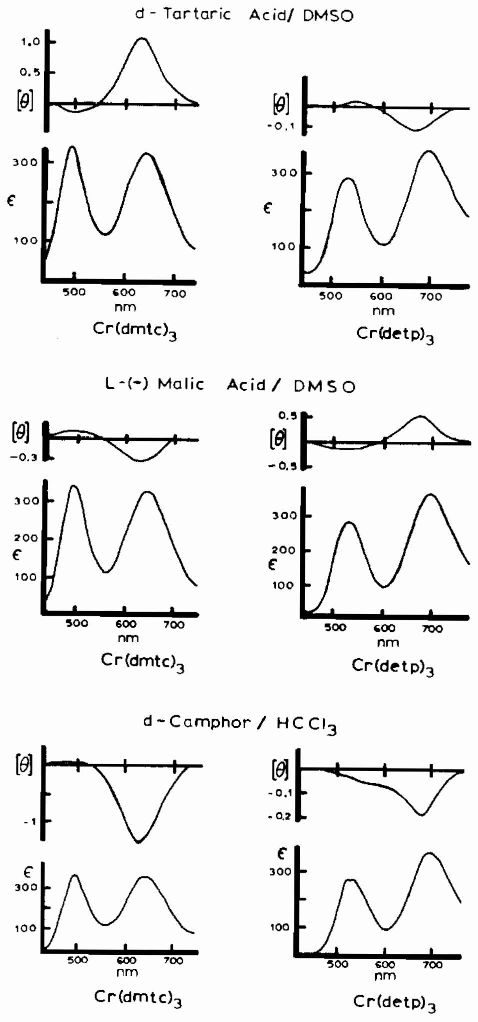


Figure 3. Electronic Absorption and Pfeiffer CD Spectra of Two ($M^{III}S_6$) Molecules in *d*-Tartaric Acid/DMSO, L-(–)-Malic Acid/DMSO, and *d*-Camphor/$HCCl_3$.

activity model would indicate that each of the six favored isomers has the Λ configuration.

d-Tartaric Acid in DMSO and L-(–)-Malic Acid in DMSO

Previous work by Kirschner[5] and co-workers demonstrated that for ionic complexes in aqueous solutions d-tartaric acid produces an excess of the complex having the Λ absolute configuration, whereas L-(–)-malic acid produces excess Δ isomers. Indeed, Figure 2 shows that we find these two acids in DMSO to induce opposite net rotational strengths for each of the neutral ($M^{III}S_6$) species. This observation is consistent with the empirical structure–Pfeiffer activity. However, it is evident (Figure 1) that any one of these two solvent systems does *not* induce the same sign of net rotational strength of magnetic parents $^4T_{2g}$(Cr) or $^1T_{1g}$(Co). This is contrary to what was found for the *d*-camphor/$HCCl_3$ solvent system, and the data are also unexpected in view of all previous experience with this model. In fact, the results contained in Figure 3 for two ($Cr^{III}S_6$) molecules in the three solvent systems, *d*-camphor/$HDCl_3$, *d*-tartaric acid/DMSO, and L-(–)-malic acid/DMSO, permit a very important conclusion to be drawn. First, note that the Pfeiffer activity of $^4T_{2g}$ of [Cr(dmtc)$_3$] at *ca.* 700 nm changes sign in going from *d*-tartaric acid/DMSO (should favor Λ) to L-(–)-malic acid/DMSO (should favor Δ). Equally important, these two solvent systems induce opposite activity in [Cr(dmtc)$_3$] and [Cr(detp)$_3$] as expected from previous experience with the two environment compounds. On comparing the above spectra to the *d*-camphor/$HCCl_3$ (favor Λ) spectra (Figure 3), one finds that the latter Λ solvent system does not give the same signs as the other Λ solvent system, *d*-tartaric acid, *i.e.,* instead of observing opposite signs for $^4T_{2g}$ of [Cr(dmtc)$_3$] and [Cr(detp)$_3$] one observes the same sign (negative).

One must conclude at this stage that the simplicity of the empirical model, which has been employed successfully for studying ionic complexes, does not apply to molecular complexes. Therefore, it appears in order to state our anticipation that great care will need to be exercised in relating Pfeiffer activity of neutral substances to molecular structure.

Finally, it is of interest to note that the Pfeiffer CD dispersions (Figures 1–3) permit one to conclude that the orbitally degenerate state, E, one of the two magnetically and electrically allowed trigonal components of $^1T_{1g}$(Co) and $^4T_{2g}$(Cr), contributes dominatingly to the observed CD intensity. This conclusion derives from the following experimental observations. First, each of the induced CD peaks is here observed to optimize at a position which is at higher energy than the solution electronic absorption bands, $^1A_1 \rightarrow {}^1T_1$(Co) or $^4A_2 \rightarrow {}^4T_2$(Cr) (see Figures 1–3, Table II). Second, polarized crystal spectra[8] have shown that the trigonal E states are the higher energy states for the magnetically allowed parents, $^1T_1$(Co) and $^4T_2$(Cr). These composite experimental observations, then, lead to the conclusion that ^1E(Co) and ^4E(Cr) are much more intense in CD than $^1A_2$(Co), and $^4A_1$(Cr), respectively. Previously studied natural CD activity of analogous *d–d* bands of strong-field Co(III) and Cr(III) complexes have similarly been found[1b] to be dominated by the E components, *e.g.,* Λ-[Coen$_3$]$^{3+}$ has a dominatingly positive ^1E band in the region of $^1T_{1g}(t_{2g}{}^5\,e_g{}^1)$.

Acknowledgements

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