

41-5; 3-quinolyl, 54978-40-4; 3-pyridyl, 29761-81-7; 2-pyridyl, 15905-71-2; 1-naphthyl, 2510-51-2; 2-naphthyl, 10237-50-0; phenyl, 2396-01-2; 2-chloroquinolyl, 95935-24-3; 4-chloroquinoline, 611-35-8; 3-chlorobenzonitrile, 766-84-7; 3-bromoquinoline, 5332-24-1; 2-chlorobenzonitrile, 873-32-5; 1-bromonaphthalene, 90-11-9; 3-chloropyridine, 626-60-8; 2-chloropyridine, 109-09-1; phthalonitrile, 91-15-6; 2-cyanopyridine, 100-70-9; 4-cyanopyridine, 100-48-1; quinoline, 91-22-5; 2,2'-bipyridyl, 366-18-7; 4-chlorobenzonitrile, 623-03-0; 4-bromobenzonitrile,

623-00-7; 4-iodobenzonitrile, 3058-39-7; 1-chloronaphthalene, 90-13-1; 1-iodonaphthalene, 90-14-2; 2-iodoquinoline, 6560-83-4; 3-iodoquinoline, 79476-07-6.

**Supplementary Material Available:** Determination of rate constants of nucleophilic attack of  $\text{PhS}^-$  and experimental variables and values (11 pages). Ordering information is given on any current masthead page.

## Spectroscopic Assignment of d-d Transitions of Achiral Metal Complexes Using Circular Dichroism: DICD of Co(III) Complexes in Sugar Solutions

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**Abstract:** Circular dichroism may be used to probe the d-d transitions of an achiral metal complex by simply adding a sugar to the aqueous solution of the complex. The interaction between the sugar and the complex is postulated to be dispersive and orientationally unselective, leading to the possibility of interpreting the induced circular dichroism in terms of the DICD (dispersion-induced circular dichroism) model. The experimental investigation of a range of Co(III) complexes of varying symmetry and in various sugar solutions supports the relevance of the DICD model and furthermore confirms that it constitutes a general method of assigning magnetic dipole allowed transitions in achiral transition-metal complexes.

Circular dichroism has proved a useful empirical tool in the study of magnetic dipole allowed d-d transitions in chiral metal complexes. Attempts at the theoretical description of the origin of this circular dichroism (CD) within the context of the independent systems approach (nonexchanging achiral d-d chromophore/chiral environment) has generated a multiplicity of distinct models,<sup>1-3</sup> each corresponding to a different physical mechanism for the induction of the CD into the achiral chromophore. This multiplicity of models can only serve to complicate any attempt to establish a *unique* relationship between the experimental spectrum and the electronic properties of the d-d chromophore. Such a relationship is crucial for the systematic exploitation of CD in the spectroscopic assignment of d-d transitions.

A unique relationship may be established in two ways. The first is through more detailed theoretical and experimental assessment of the models for chiral complexes in order to elicit the conditions under which each one may be expected to dominate, if more than one mechanism is important. We shall in fact pursue this approach in a forthcoming publication. The second method, and the one which we shall discuss in detail in this paper, is the exploitation of a physical limit, which is theoretically and experimentally realizable, in which only one of the models survives in leading to a nonvanishing CD.

The theoretical limit in which only one mechanism survives is the limit of free rotation between the achiral chromophore and the chiral inducer. The experimental realization of this limit is the measurement of the induced CD of an achiral complex in solution with a chiral solute with which it does not specifically associate. In such cases, the achiral chromophore and the chiral inducer have no orientational correlation. This is theoretically realizable through rotational averaging where all relative orientations

are assumed equally probable. All so-called first-order terms (i.e., resulting from first-order perturbation theory), which are the conceptual basis of both static and dynamic coupling mechanisms,<sup>1,2</sup> rigorously vanish in this limit. However, second-order terms survive the averaging even within the dipole approximation, leading to the contributions which are characteristically referred to as the DICD (dispersion-induced CD) terms.

The persistence of induced CD of the achiral chromophore under these conditions potentially extends the utility of chiral spectroscopy to achiral chromophores without the need to introduce a chemically attached chiral center and without the need to apply static fields to the sample. In this context, it is worth pointing out that MCD studies (in which achiral chromophore become CD active through perturbation by a static magnetic field) effectively probe an electric dipole character; we shall see that the CD induced by another chiral molecular species is capable, however, of directly probing the magnetic dipole character.

The observation of the induced CD of achiral species in chiral solvents or in solution with chiral additives has been reported by a number of workers.<sup>4-9</sup> Initial speculation suggested that definite association (with a fixed relative orientation) between the achiral and chiral moieties was a prerequisite for the induction of chirality into the chiral species; however, the experiments of Hayward and Totty<sup>6</sup> and Axelrod et al.<sup>7</sup> convincingly demonstrated that this was not the case. Subsequent theoretical studies dealing directly with the development of the DICD model<sup>10</sup> and with somewhat more general symmetry arguments<sup>11</sup> confirmed that transmission of chirality between freely rotating systems is both possible and, in the case of dispersive coupling, allowed in the dipole approximation.

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The direct exploitation of DICD as a tool for spectroscopic assignment of the d-d transitions of achiral metal complexes depends ultimately on (i) the sensitivity to the symmetry of the transitions of the achiral chromophore and (ii) the ability to find readily available chiral inducers which lead to a practical realization of the assumptions inherent in the DICD model for a wide range of complexes. In this paper, we present the results of a series of experiments in which these two factors are investigated in a relatively systematic way, i.e., for a series of complexes with similar electronic configuration (i.e., constant metal ion) but a range of point group symmetries (i.e., differing ligand environments) and for a series of inducers that are relatively unspecific with respect to orientational correlation with the achiral complexes.

### Theoretical Considerations

It is possible to appreciate the essential features of the DICD model without discussing all the details of the theory; the full derivation is presented elsewhere.<sup>10</sup> We shall start instead with a brief discussion of the quantities that are actually measured and then discuss the expressions for these quantities as given in the context of the DICD model.

The achiral chromophores investigated in this work are a series of Co(III) complex cations, with simple sugars constituting a set of chiral inducers. The sugars do not absorb until the far ultraviolet and therefore are spectroscopically transparent (in both the normal absorption and the CD) over the entire range of interest for a wide variety of metal complexes. The CD spectrum of a Co(III) ion/sugar mixture in aqueous solution is referred to as the DICD spectrum for the following reasons. The DICD bands appear at the transition energies of the achiral chromophore, i.e., the Co(III) ion. They vanish in the absence of the sugar and are weak compared with the CD intensities of intrinsically chiral chromophores; they must therefore be the direct result of the Co(III)/sugar coupling. The absorption spectrum of the Co(III) ion is identical in the presence or absence of the sugar, suggesting furthermore that the coupling is relatively weak. In the DICD model, it is postulated that the coupling is purely dispersive.

The major assumptions of the DICD model are the neglect of electron exchange between the Co(III) ion and sugar moieties (an uncontroversial assumption) and the equal probability of all relative Co(III)/sugar orientations (the DICD approach employing an unweighted rotational averaging procedure which is physically realizable through either a temporal or a configurational average). The latter assumption is best justified through investigating the orientational dependence of the unaveraged second-order terms for the induced CD a nontrivial task which will be explicitly discussed in a later publication. However, only in cases where there is a dramatic dependence on orientation (which is unlikely) or where the association is sufficiently specific to lead to only a small number of dominant relative configurations (which can be tested empirically by suitable variation of inducers) would we expect this assumption to become untenable.

In order to discuss the theoretical expression for the DICD intensity in the context of the DICD model, it is necessary to establish a notation for the excited states of both the achiral and chiral systems, as dispersive coupling involves the coupling of virtual excitations on the two centers. Let the ground state of the Co(III) ion be represented by  $|0\rangle$  and the excited d configuration by  $|d^*\rangle$  such that the d-d transition under consideration (i.e., at whose transition energy the DICD band appears) is  $|0\rangle \rightarrow |d^*\rangle$ . The dispersive coupling will be through some other excited (virtual) state, denoted by  $|e^*\rangle$ , of the Co(III) ion which is strongly electric dipole allowed from the ground state.  $|0'\rangle$ ,  $|u^*\rangle$ , and  $|v^*\rangle$  similarly represent the ground and two excited states of the sugar. The DICD intensity appearing at the  $|0\rangle \rightarrow |d^*\rangle$  transition energy of the Co(III) ion, assumed to be magnetic dipole allowed and electric dipole forbidden, may be written in the form

$$R_{d^*} = \sum_{e^*} R_{d^*}(e^*) \quad (1)$$

where

$$R_{d^*}(e^*) = r_{AC}^{-6} A(d^*, e^*) C_{\text{eff}} \quad (2)$$

In this expression,  $r_{AC}$  is the separation of the origins of the Co(III)/sugar moieties and  $A(d^*, e^*)$ , which we shall refer to as the  $A$  factor (the achiral factor), is a property only of the Co(III) ion.  $C_{\text{eff}}$ , the  $C$  factor (chiral factor), is a property of the chiral species but also indirectly of the energy of the  $d^*$ ,  $e^*$  states of the achiral species.

It is the  $A$  factor which is of most interest to us here, for it depends directly on the excitation properties of the Co(III) ion. It has the explicit form

$$A(d^*, e^*) = \text{Im } \mathbf{m}^{0d} \cdot \boldsymbol{\mu}^{de} \times \boldsymbol{\mu}^{e0} \quad (3)$$

where  $\mathbf{m}^{0d}$  is the magnetic dipole transition moment ( $0|\mathbf{m}|d^*$ ) of the  $|0\rangle \rightarrow |d^*\rangle$  transition.  $\boldsymbol{\mu}^{de}$  and  $\boldsymbol{\mu}^{e0}$  are the electric dipole transition moments of the  $|d^*\rangle \rightarrow |e^*\rangle$  and  $|e^*\rangle \rightarrow |0\rangle$  transitions, respectively. For a given sugar, we initially assume that  $C_{\text{eff}}$  is relatively insensitive to the Co(III) ion transition energies (a point we return to later), the  $A$  factor will determine the form of the DICD spectrum, the effect of  $C_{\text{eff}}$  merely being to multiply the whole spectrum by a positive or negative constant characteristic of the sugar. The DICD spectrum will then be a direct monitor of the magnetic dipole allowed transitions with intensities of each band proportional to the  $A$  factor characteristic of that transition. The DICD intensities are therefore totally unrelated to the normal absorption intensities and will thus yield information unobtainable from the normal absorption spectrum. In addition, as will be discussed later, those transitions arising from a splitting of a degeneracy under a higher symmetry usually have  $A$  factors of opposite sign, so that they will be clearly distinguishable in the DICD spectrum.

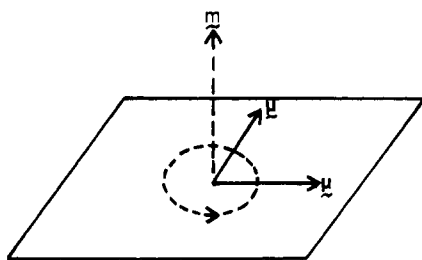
The symmetry restrictions inherent in the form of the  $A$  factor lead to the selection rules which are the basis of the application of the DICD technique to spectroscopic assignment. In the jargon of the generalized selection rules,<sup>12</sup> these rules derive from the vector form of the operator product ( $\mathbf{m} \cdot \boldsymbol{\mu} \times \boldsymbol{\mu}$ ) and the usual state selection rules for each individual matrix element. The former require the moments to be mutually orthogonal (or at least have noncoplanar components) and coupled with the state selection rules lead to the allowed symmetries of  $|d^*\rangle$  and  $|e^*\rangle$  as summarized in Table I for the point groups and states of interest to this paper, assuming a totally symmetric ground state.

These full selection rules are only useful if the charge-transfer states of the complex have been studied in sufficient detail (i.e., if their symmetry, intensities, and transition energies are known) and if  $C_{\text{eff}}$  is largest for states  $|e^*\rangle$  relatively close energetically to the excited d configuration  $|d^*\rangle$ . Detailed information regarding the charge-transfer states is unfortunately not generally available, so that the practical implementation of the full selection rules is restricted to those complexes for which the charge-transfer manifold is sufficiently well characterized and for which  $C_{\text{eff}}$  is well-behaved. The definition of the latter is discussed later in this section.

Fortunately, however, it is still possible to exploit the selection rules in a somewhat less detailed way. The polarization of the  $|0\rangle \rightarrow |d^*\rangle$  transition in the DICD context refers to the polarization of its intrinsic magnetic transition moment. If this moment has  $\alpha$  polarization ( $\alpha = x, y, z$ ), then it will involve (from the definition of a magnetic moment as an angular momentum about the axis defining its polarization) a "circulation" of charge around the  $\alpha$  axis, i.e., will (for systems dominated by  $\sigma$ -type bonding) be most affected by substituents in the ( $\beta\gamma$ ) plane perpendicular to the  $\alpha$  axis. Noting that the nature of the  $A$  factor requires the electric dipole transition moments  $\boldsymbol{\mu}^{de}$  and  $\boldsymbol{\mu}^{e0}$  to be directed in this same plane (see Figure 1), they too will be most affected by substituents in this plane. This results in a qualitative correlation of the DICD intensity of an  $\alpha$  (magnetically) polarized transition with the chemical nature of the ( $\beta\gamma$ ) plane. A simple example of this is a series of  $C_{4v}$  metal complexes differing only in axial substitution (i.e., along the symmetry  $z$  axis). The  $z$ -polarized (magnetic) d-d transition should have a DICD of roughly constant intensity throughout this series, whereas transitions of other po-

**Table I.** Selection Rules for the d-d Transitions Arising from Bands of  $T_{1g}$ ,  $T_{2g}$  Parentage for a Totally Symmetric Ground State

point group	symmetry of d-d transition of parentage		allowed moments and polarization	symmetry of allowed virtual state [ $e^*$ ]
	$T_{1g}$	$T_{2g}$		
$O_h$	$T_{1g}$		$[R_x, R_y, R_z]$	$T_{1u}$
$D_{4h}$	$A_{2g}$	$T_{2g}$	$R_z$	$E_u$
	$E_g$		$[R_x, R_y]$	$E_u, A_{2u}$
$D_{2h}$		$B_{2g}$	$[R_x, R_y]$	$E_u, A_{2u}$
	$B_{1g}$	$E_g$	$R_z$	$B_{2u}, B_{3u}$
	$B_{2g}$		$R_y$	$B_{1u}, B_{3u}$
	$B_{3g}$		$R_x$	$B_{1u}, B_{2u}$
$D_{3d}$		$A_g$	$R_y$	$B_{1u}, B_{3u}$
		$B_{2g}$	$R_x$	$B_{1u}, B_{2u}$
		$B_{3g}$	$R_z$	$E_u$
$C_{4v}$	$A_{2g}$	$A_{1g}$	$[R_x, R_y]$	$A_{2u}, E_u$
	$E_g$		$R_z$	$E$
$C_{42v}$	$A_2$	$E_g$	$[R_x, R_y], [x, y]$	$E, A_1$
	$E$	$B_2$	$[R_x, R_y], [x, y]$	$E, A_1$
	$B_1$	$E$	$R_y, x$	$A_1, B_1$
$C_s$	$B_2$		$R_x, y$	$A_1, B_2$
	$A_2$	$A_1$	$R_z$	$B_1, B_2$
		$B_2$	$R_x, y$	$A_1, B_2$
		$A_2$	$R_z$	$B_1, B_2$
$C_s$	$A'$		$R_y, x, z$	$A', A''$
	$A''$		$R_y, R_z, y$	$A', A''$
	$A''$		$R_x, R_z, y$	$A', A''$
		$A'$	$R_y, x, z$	$A', A''$
		$A''$	$R_x, R_z, y$	$A', A''$
		$A''$	$R_x, R_z, y$	$A', A''$

**Figure 1.** Diagrammatic representation of the relative directions of the transition moments comprising the A factor. Note that the plane defined by the two electric moments also contains the transient "current loop" defining the magnetic moment.

larizations may be expected to be more sensitive to the axial substitution. We shall exploit this result later.

The explicit form for  $C_{eff}$  may be written

$$C_{eff} = \sum_{\substack{u^*, v^* \\ u^* < v^*}} \mu^{ou} \cdot \mu^{uv} \times \mu^{vo} f_i(d^*, e^*, u^*, v^*) \quad (4)$$

where  $\mu^{uv}$  is the electric dipole transition moment of the  $|u^* \rangle \rightarrow |v^* \rangle$  transition of the sugar (i.e., the chiral inducer). The  $f_i$  is an energy factor having the full form

$$f_i(d^*, e^*, u^*, v^*) = (1/6) \Delta_{vu} [\epsilon_1 + \epsilon_{11} + \epsilon_{111}] \quad (5)$$

where

$$\epsilon_1 = \epsilon_d / [\epsilon_{ev} \epsilon_{eu} (\epsilon_v + \Delta_{ed}) (\epsilon_u + \Delta_{ed})] \quad (6)$$

$$\epsilon_{11} = [\epsilon_e + 2\Delta_{ed} + \epsilon_{vu}] / [(\epsilon_v + \Delta_{ed}) (\epsilon_u + \Delta_{ed}) (\epsilon_e^2 - \Delta_{vu}^2)] \quad (7)$$

$$\epsilon_{111} = [2\epsilon_e + \Delta_{ed} + \epsilon_{vu}] / [(\Delta_{vu}^2 - \Delta_{ed}^2) \epsilon_{ev} \epsilon_{eu}] \quad (8)$$

and, if  $\epsilon_i$  is the transition energy of state  $|i^* \rangle$  relative to the relevant ground state,

$$\epsilon_{ij} = \epsilon_i + \epsilon_j, \quad \Delta_{ij} = \epsilon_i - \epsilon_j \quad (9)$$

For assignment purposes, it would be of great assistance if  $f_i$  had a relatively simple inverse dependence on  $\Delta_{ed}$ , the energy gap between the excited d state and the virtual state of the complex ion. This would restrict consideration of the A factors to those involving only low-lying charge-transfer states, which are at least potentially accessible to investigation. Unfortunately the general behavior of the energy term is somewhat obscured by its complexity and its dependence on the details of the excitation manifold of the chiral inducer (i.e., the sugar). However, some general conclusions may be drawn. For the first two contributions ( $\epsilon_1$  and  $\epsilon_{11}$ ), we have that  $\epsilon_1 > 0$  and  $\epsilon_{11} > 0$  provided  $\epsilon_e > \Delta_{vu}$ . In both cases, a small  $\Delta_{ed}$  is favored through the appearance of terms of the form  $(\epsilon_v + \Delta_{ed})$  in the denominator. Thus a general trend toward favoring a small  $\Delta_{ed}$  for a large  $f_i$  may be expected if these two contributions dominate the energy expression. This is precisely the sort of behavior that would lead to the dominance of the low-lying charge-transfer states in the summation over the virtual manifold of the achiral species.

The relative importance of  $\epsilon_{111}$  is difficult to gauge, having an energy difference denominator  $(\Delta_{vu} - \Delta_{ed})$  which determines the sign and also would lead to large contributions if  $\Delta_{vu} \approx \Delta_{ed}$ . However, this condition could only be achieved "accidentally", so that this contribution does not have a simply predictable dependence on  $\Delta_{ed}$  because of our ignorance of the details of the excitation manifold of the sugar.

We shall, in fact, resort to an empirical test of which of these contributions dominate the energy factor. Domination by the terms  $(\epsilon_1 + \epsilon_{11})$  leads to a behavior which may be summarized by writing  $C_{eff}$  in the following form:

$$\bar{C}_{eff} \sim K / (k + \Delta_{ed})^2 \quad (10)$$

In this expression,  $K$  and  $k$  are constants for a given chiral inducer ( $k$  positive,  $K$  positive or negative). The magnitude and sign of  $K$  are a function of the particular sugar but should be approximately transferable for a range of complexes. This is unlikely to be the case for the contribution  $\epsilon_{111}$ , for which the behavior may be expected to be more erratic. We shall see that the experiments reported later in this paper suggest that the form of eq 10 provides a good basis for interpretation of the results, suggesting dominance of the  $(\epsilon_1 + \epsilon_{11})$  contribution to the energy factor.

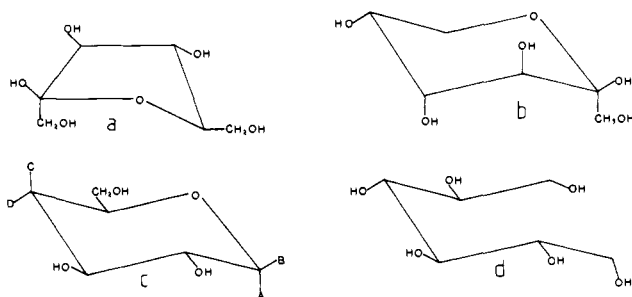
### Practical Considerations

**Choice of Chiral Inducers.** Crucial to the practical implementation and utility of the DICD technique is the availability of chiral inducers suitable for a wide range of metal complexes. Sugars are, in fact, ideal as chiral inducers for metal complexes in aqueous solution for several reasons. They are spectroscopically inactive until the far ultraviolet, readily water soluble (enabling high inducer concentrations), readily available in optically pure form, cheap, and relatively inert with respect to ligand exchange for a wide range of complexes. The particular compounds selected as inducers are the commercially available monosaccharides (fructose, galactose, and glucose) and the sugar derivative sorbitol, which is derived from glucose but not restricted to a ring structure. The sugars exist in isomeric forms, and the relative amounts of the forms at 30 °C are given in Figure 2 along with their structures, as determined by Angyal.<sup>13</sup> Space-filling models highlight the almost spherical shape of the molecules, with the hydroxyl groups sticking out from the sphere. Thus it would seem unlikely that the sugars would interact specifically with the complexes through any particular sugar site.

An exception to this lack of specificity has been reported by Reeves<sup>14</sup> in a study of sugars in cuprammonium solutions. The sugars are capable of binding to  $Cu(NH_3)_4^{2+}$  ions through two hydroxyl groups which are less than 3.45 Å apart and on adjacent carbons on the sugar chain. The binding is directly to the copper ion and is strongest for glucose which has two pairs of hydroxyl groups satisfying the above geometric constraints. If such a

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(14) Reeves, R. E. *J. Am. Chem. Soc.* 1949, 71, 215.



**Figure 2.** Structures of the sugars used as chiral inducers. Relative concentrations of the dominant conformers as determined by Angyal<sup>13</sup> are given as follows:  $\beta$ -D-fructose 25% [a], 65% [b]; D-galactose 64% [c: B = OH, C = OH], 30% [c: A = OH, C = OH]; D-glucose 62% [c, B = OH, D = OH], 38% [c: A = OH, D = OH]; D-sorbitol [d]. For the [c] structures, the unspecified letters are hydrogens.

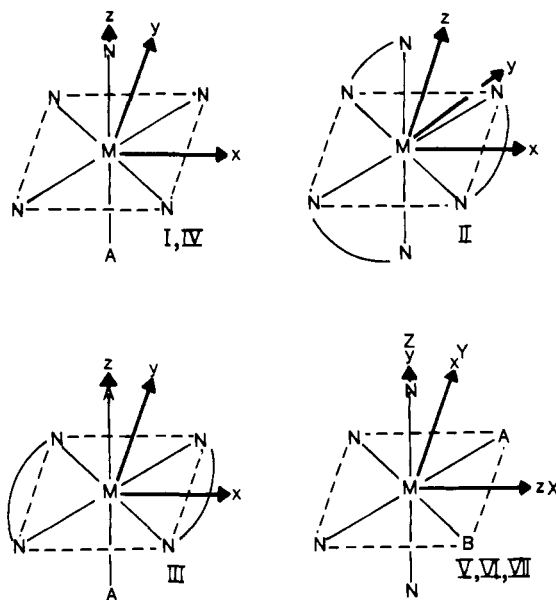
specific binding to the metal occurs, one might expect a significant change in the absorption spectrum and also a marked dependence of the CD on the nature of the sugar. We shall see later that this does not seem to be the case in the systems studied here.

One complicating factor in the use of the sugars is the choice of the origin in the determination of the  $r_{AC}$ . This will arise whenever inducers with a number of chiral centers are used. We shall assume that  $C_{eff}$  for a system like a sugar with no low-lying transitions may be considered as containing additive contributions from each chiral center; it follows that the nearest chiral center at any time will determine the effective value of  $r_{AC}$ . The overall  $C_{eff}$  may then be considered as an average acting at an average distance. It is important to note that the inverse sixth dependence of this average distance (denoted  $r_{AC}$  for convenience) leads to quite a marked dependence of the DICD magnitude on distance: changing the distance by a factor of  $1/2$  changes the DICD by an order of magnitude. This highlights the need for relatively high inducer concentrations in order to get a reasonable DICD signal, and hence of the inducer being readily soluble.

**Choice of Complexes.** Substituted cobalt(III) amine complexes were selected in this study for the following reasons. They are known to be relatively stable in solution, so that reactions with the sugars are unlikely to occur; there is at least some basic information about the d-d spectroscopy, although the knowledge is far from complete; selected halo-, aqua-, and carbonato-substituted complexes give a range of symmetries of the achiral chromophores.

Co(III) has a  $d^6$  configuration and is almost exclusively low spin in its complexes, leading to a totally symmetric ground state. Under octahedral symmetry, the lowest energy visible absorption band is of  ${}^1A_{1g} \rightarrow {}^1T_{1g}$  symmetry, which is electric dipole forbidden and magnetic dipole allowed. It is in fact this parent band that we shall monitor in the DICD studies, as it splits into separate  $A_2$  and E components when the z axis becomes distinguishable, with the E splitting into separate  $B_1$  and  $B_2$  components on further lifting the x,y degeneracy. To monitor the potential spectral changes as the symmetry of the complexes is systematically reduced, the following complexes (with the symmetries in parenthesis) were studied: I =  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  ( $O_h$ ); II =  $[\text{Co}(\text{en})_3]\text{I}_3$  ( $D_3$ ); III = *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$  ( $D_{2h}$ ); IV =  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Br}_2$  ( $C_{4v}$ ); V = *cis*- $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]_2(\text{SO}_4)_3$  ( $C_{2v}$ ); VI =  $[\text{Co}(\text{NH}_3)_4\text{CO}_3]_2\text{SO}_4$  ( $C_{2v}$ ); VII = *cis*- $[\text{Co}(\text{NH}_3)_4\text{H}_2\text{OCl}]\text{Cl}_2$  ( $C_2$ ). Complex II was used in racemic form and, being kinetically inert under the experimental conditions, acts as an achiral complex of  $D_{3d}$  symmetry.

The symmetry labels that are used in this work are based on the actual symmetries of the complexes in terms of the (xyz) axis systems defined in Figure 3, with the usual point group conventions. The relative energy ordering of the excited states is usually based on holohedrized symmetries (effectively adding an inversion to the real symmetry; e.g.,  $C_{2v}$  becomes  $D_{4h}$ ) because the theoretical splittings in the context of simple crystal field or angular overlap models are sensitive only to the average of the splitting parameters of each mutually trans pair of ligands (and hence effectively replacing them by two identical "averaged" species). The holohedral



**Figure 3.** Symmetry labels for the various complexes discussed in the text, with (xyz) denoting the system choice for the actual symmetry and (XYZ) for the holohedrized symmetry. The complexes are labeled as follows: I (A =  $\text{NH}_3$ ); II (N-N = ethylenediamine); III (A =  $\text{Cl}^-$ ); IV (A =  $\text{Br}^-$ ); V (A = B =  $\text{H}_2\text{O}$ ); VI (AB =  $\text{CO}_3^{2-}$ ); VII (A =  $\text{H}_2\text{O}$ , B =  $\text{Cl}^-$ ).

symmetry notation will therefore be in terms of an axis system (XYZ) which is different, for the lower symmetries, from the (xyz) system. This is also illustrated in Figure 3. The holohedrized symmetry is appropriate for normal absorption for which, as we shall see, there is at most a twofold splitting into the A and E components of the higher holohedrized symmetry visible in the spectrum. However, the DICD spectrum is able to resolve the further splitting of the E band for lower symmetries, and thus the holohedrized symmetry is inappropriate.

**Method.** The CD spectra were measured on a JASCO-500C spectropolarimeter with the DP-500N data processor attachment. The solutions were made up to be 1.0 M in sugar and  $\sim 0.3$  M in the complex in distilled water. Temperature was maintained at  $20 \pm 2$  °C. All complexes were recrystallized prior to use, and the sugars were used as commercially available. Solutions were run immediately after preparation, and all DICD spectra were reproducible on newly prepared solutions. No measurable differences were obtained when baselines for no sample, a pure sugar solution, or the pure complex and pure sugar solutions in series (in different cells) were used. Concentration-dependent studies on the *cis*-diaquatetramine indicated an approximately linear dependence, consistent with earlier studies on organic systems.<sup>6</sup>

### General Features of the Spectra

**Normal Absorption.** The normal absorption spectra for the various complexes are shown in Figure 4. They are generally weak, with intensities characteristic of electric dipole forbidden transitions, even for those complexes having a sufficiently low symmetry for the d-d transitions to become formally electric dipole allowed. The intensities are therefore predominantly vibronically induced. In fact, the normal absorption spectra of all the complexes are remarkably similar in their overall character, differing only in the position and intensity of the absorption maxima, with little hint of the underlying symmetry variation of the complexes. Only the *trans*-dichloro complex differs significantly from the single, broad and relatively structureless bands characteristic of the  $T_{1g}$  octahedral normal absorption, having the  $A_2$ , E bands of the  $T_{1g}$  parentage completely separated. The  $T_{2g}$  bands, details of which are not considered in this work, are also similar. The normal absorption is therefore relatively insensitive to symmetry changes, and its use in assignment requires extensive polarization studies and vibronic coupling analyses.

Addition of the sugars has no effect on the normal absorption. There is no change in the energy or intensity of the bands in the

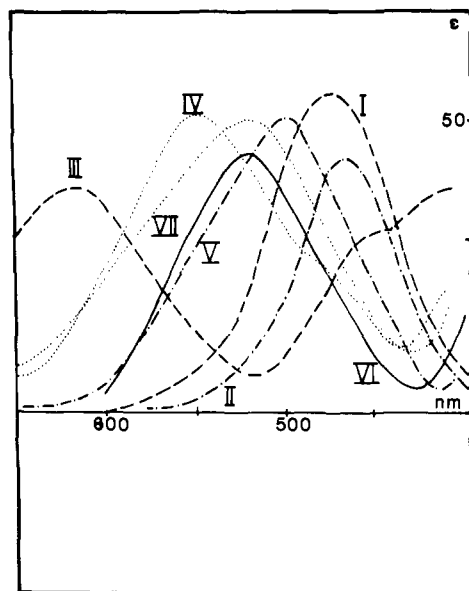


Figure 4. Normal absorption spectra of the various complexes. The values of  $\epsilon$  are per mole of Co(III).

d-d region, even at the relatively high sugar concentrations used in the DCD studies. This fortunately confirms that the interaction between the sugar and the complex is relatively weak, a feature that is vital to the relevance of the DCD model.

**DICD Spectra.** In contrast to the normal absorption, the DICD spectra vary dramatically as a function of the symmetry of the complexes. This symmetry dependence is highlighted in Figure 5, in which the DICD of the various complexes are shown collectively in solution with fructose. At the simplest level, there are clear differences in the number and magnitude of the peaks arising from the parent  $T_{1g}$  band. The number of peaks is, in each case, consistent with that predicted on symmetry grounds based on a magnetic dipole selection rule; i.e.,  $O_h$  has a single band;  $D_{3d}$  (close to  $O_h$ ) has one large peak, with a hint of a smaller one of opposite sign; the  $C_{4v}$  complex has two peaks; the  $D_{2h}$  complex, with an approximately  $D_{4h}$  chromophore, has two large peaks and a hint of a third; and finally, the  $C_{2v}$ ,  $C_s$  complexes all exhibit three clearly discernible bands.

This work is concentrated on the  $T_{1g}$  band; the  $T_{2g}$  band, which under octahedral symmetry is both electric and magnetic dipole forbidden, appears to have negligible DICD activity in any of the sugars, although there does appear to be a small structureless DICD band corresponding to the  $T_{2g}$  transition in the  $D_{3d}$ ,  $D_{2h}$ , and  $C_{2v}$  complexes, for which some components (see Table I) of the  $T_{2g}$  transition become formally magnetic dipole allowed. However, we would expect these to be considerably weaker than the  $T_{1g}$  components, which is indeed the case, and the  $T_{2g}$  band will therefore not be discussed further in this work.

The DICD spectra for the individual complexes in the various sugars are given in Figure 6. The variation as a function of the inducer is consistent with that described by eq 10 in that the DICD spectra of a given complex in the various sugars are related by a multiplicative constant (positive or negative) characteristic of the sugar. It follows that it is usually sufficient to compare the DICD spectra of the range of complexes in a single sugar, with the other sugars serving as a check for any specificity of association. In the comparison of the DICD of the various complexes in fructose (Figure 5), it becomes apparent that the splitting of degeneracies due to symmetry lowering invariably leads to bands of opposite sign, a factor which is vital to a clear separation of the component transitions in the DICD spectra. In order to rationalize why this is so, we digress briefly to a discussion of the natural CD of intrinsically chiral complexes, for which this behavior is also observed.

We consider here only a qualitative argument, as a rigorous rationalization would require explicit functional definitions of the various states involved. CD is a property which depends crucially

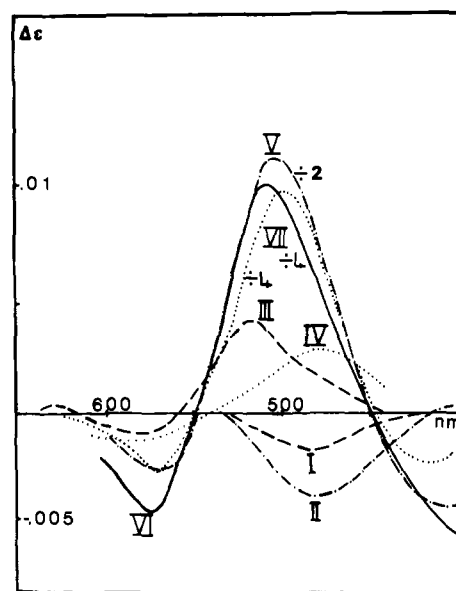
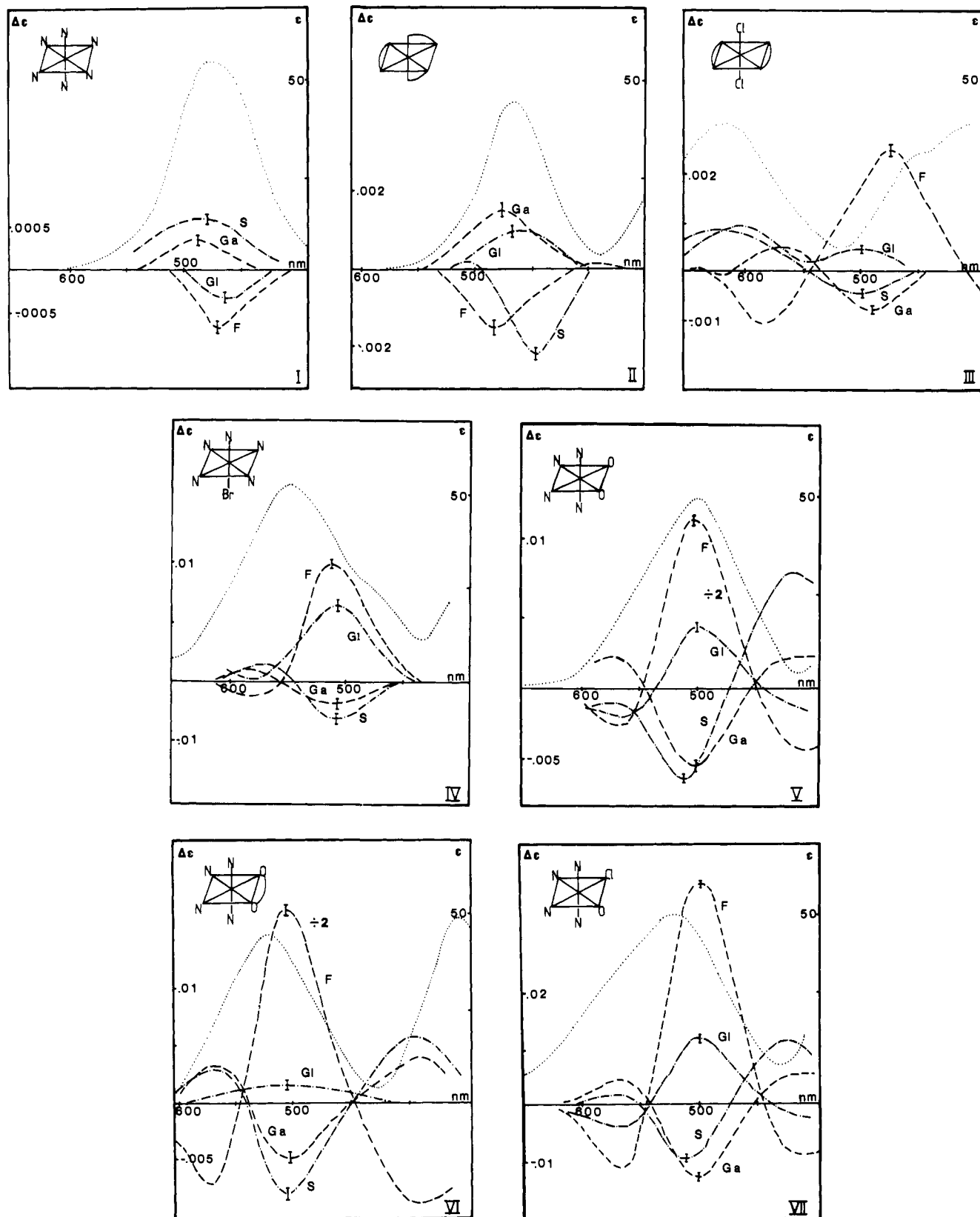


Figure 5. DICD spectra of the various complexes in fructose (1.0 M). The  $\Delta\epsilon$  are given per mole of Co(III).

on the degree of asymmetry of the molecule. For example, achiral molecules have a sufficiently low degree of asymmetry to ensure that the CD vanishes entirely. For chiral molecules, the only possible symmetry elements are proper rotations, and examples of such groups in decreasing degree of asymmetry (i.e., increasing order of symmetry) are  $C_1$ ,  $C_n$ ,  $D_n$ , and  $O$ . We may expect that the magnitude of CD bands for a molecule may increase (qualitatively) with the degree of asymmetry of its covering point group, whereas its potential for having a degenerate state decreases with the degree of asymmetry. It follows that a twofold splitting of a degeneracy must always lead to bands of opposite sign, each stronger in magnitude than the originally degenerate band. For example, consider the case in which we go gradually from  $D_4$  to  $O$  symmetry. The A and E bands under  $D_4$  coalescing to give the parent  $T_{1g}$  under  $O$  will individually have CD strengths of magnitude greater than the parent band in the higher symmetry; in the limiting case as the splitting approaches zero, the two bands can only combine to give a band of lower CD magnitude if they are of opposite sign. We shall refer to that component having a CD of the same sign as the fully degenerate CD band as the major component, whereas the other will be referred to as the minor component.

In the application to the DICD case, we may simply extend the argument presented above for the chiral complexes in the following way. If we treat the chiral inducer simply as a medium which destroys the improper axes of the achiral species (not unlike the lowering of the symmetry of a guest molecule in a host lattice by the crystal symmetry), we may define an "effective" symmetry of the achiral species in which only the proper symmetry elements are retained; this "effective" symmetry will of course be chiral, so that the DICD may be considered as equivalent to the CD spectrum expected for a complex with the "effective" symmetry. (This in fact gives a simple picture of the DICD phenomenon.) As all degeneracies result from the proper rotation axes (except for certain  $S_n$  groups), the "effective" symmetry will have all the degeneracies of the original achiral group. Examples of such "effective" symmetries are "O" for  $O_h$ , " $C_2$ " for  $C_{2v}$ , " $D_3$ " for  $D_{3d}$ , and so on. The extension of the argument of the previous paragraph then extends naturally to the interpretation of the DICD as the natural CD of the "effective" symmetry.

Thus far we have discussed the most obvious features of the DICD spectra, viz., the agreement of the number of bands with that expected for the symmetry of the achiral chromophore and the opposite signs of bands arising from a split degeneracy. This enables an *approximate* determination of the component transition energies; however, the band maxima/minima have relatively large uncertainties due to the well-known possibility of mutual can-



**Figure 6.** DCD spectra of each complex in the various sugars: F = fructose; Ga = galactose; Gl = glucose; S = sorbitol. The normal absorption appears as the dotted curve in each case. Both the  $\epsilon$  and the  $\Delta\epsilon$  are per mole of Co(III).

cellation inherent in CD spectra when contiguous bands have opposite signs. The final stage of assigning the symmetry of the excitations is discussed in the next section.

#### Assignment of the Transitions

In assessing the potential of DCD as a tool for spectroscopic assignment, we shall consider the complexes in three separate groups: (i) those with at least an approximate octahedral sym-

metry (I, II), (ii) those with a definite unique  $z$  axis but retaining at least an approximate ( $xy$ ) degeneracy (III, IV), and (iii) those with no remaining degeneracies (V, VI, VII). The assignment for groups i and ii have been established independently (see, for example, ref 15-17), so that our results consolidate the assignment;

for group iii, however, the DICD acts to complement earlier studies in providing a complete assignment of all three transitions, illustrating most clearly the potency of the procedure. We discuss these three groups of results in turn.

(i)  $\text{Co}(\text{NH}_3)_6^{3+}$  and  $\text{Co}(\text{en})_3^{3+}$ . The DICD spectrum of the octahedral complex is a singly triply degenerate band, of relatively low intensity compared to the other DICD spectra as expected from the discussion of the preceding section. In the  $D_{3d}$  (racemic) complex, the DICD spectrum is very similar in shape to the natural CD of the resolved complex. This is not unexpected, as the "effective" symmetry of the racemate in the sugar is the same as the real symmetry of a single enantiomer. (The kinetic inertness of the enantiomers precludes an equilibrium shift mechanism for the origin of the induced CD characteristic of the so-called Pfeiffer effect.<sup>18</sup>) The parent  $T_{1g}$  band splits into an E band at about 480 nm and an  $A_2$  band at about 450 nm. The actual energy splitting is difficult to estimate because of the extensive cancellation of the oppositely signed E and  $A_2$  bands.

Which of the bands dominates the DICD intensity depends on the nature of the inducer, a rare instance of some sort of specific inducer dependence in the results. It could merely be the result of the form of  $C_{\text{eff}}$  of eq 10 being too simplistic for these two complexes. Thus in fructose and galactose, the E band is dominant, with the weak  $A_2$  band visible only for fructose. For sorbitol and glucose, the A band appears to dominate, completely swamping the E band in glucose.

The E band at about 500 nm has a sign pattern (−+ +) for the sugars (fructose, glucose, galactose, sorbitol), that for glucose being estimated as opposite to that of the  $A_2$  band. When this E band is further split in the lower symmetry complexes, the minor component remains at about 500 nm, with a DICD band sign pattern exactly reversed (+ + −) in the four sugars. This band, which we shall refer to as the "amine" band, will prove to be of crucial importance in assigning the spectra of the lower symmetry complexes.

(ii)  $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$  and  $\text{trans}-[\text{Co}(\text{en})_2\text{Cl}_2]^+$ . These two complexes may be considered together in that the halogen substitution is along the unique axis ( $z$ ), so that the ( $xy$ ) degeneracy is exactly retained in the bromo complex and approximately in the chloro complex. The higher energy transition has been assigned as  $A_2$  on the basis of vibronic coupling and polarization arguments.<sup>16,17</sup> In the normal absorption, the  $A_{2g}$  band appears as a shoulder on the  $E_g$  band in the bromo complex, but the two are well split in the chloro complex, the latter being a general characteristic of trans-substituted complexes.

In the DICD spectra, the bands are well separated, including a clear separation of the  $A_{2g}$  and the unresolved components of the octahedral parent  $T_{2g}$  bands (which overlap in the normal absorption) in the trans complex. The band at 500 nm, i.e., the  $A_{2g}$  band, is the characteristic "amine" band mentioned earlier. It has a  $z$ -polarized magnetic transition moment, and thus the A factor depends primarily on the properties of the ( $xy$ ) plane, as previously discussed. This plane contains only nitrogen coordination, and thus we may expect it to have an analogue (as

the minor component of the E band) in the hexaammine and tris(en) complexes. (Note that the  $E_g$  and E notation are with respect to quite different axis systems for the different complexes.) We may therefore consider the appearance of this "amine" band as diagnostic of an approximate "amine" plane. The  $E_g$  band in these complexes however depends directly on the halogen substitution, being (relative to the  $A_{2g}$  band) stronger in the chloro than in the bromo complex.

(iii)  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{3+}$ ,  $[\text{Co}(\text{NH}_3)_4\text{CO}_3]^+$ , and  $\text{cis}-[\text{Co}(\text{NH}_3)_4\text{H}_2\text{O Cl}]^{2+}$ . In these complexes, the degeneracy has been completely resolved. The normal absorption in each case is a single, broad, structureless band; however, the DICD spectra are well resolved and very similar for the three complexes. For the  $C_s$  complex, the aqua and chloro ligands may be taken as approximately equivalent, giving an approximate  $C_{2v}$  symmetry; the same axis system is therefore used in all three cases (see Figure 3).

By considering holohedrized symmetries, Hawkins<sup>15</sup> deduces the relative energy ordering of the components of the parent  $T_{1g}$  band in these types of complexes. The  $C_{2v}$  complex (system  $xyz$ ) under holohedral symmetry becomes  $D_{4h}$  (system  $XYZ$ ), where  $X = z$ ,  $Y = x$ ,  $Z = y$ . The postulated assignment is then given as  $A_{2g} (D_{4h}) < E_g (D_{4h})$  in energy ordering; i.e.,  $B_1 (C_{2v}) < A_2 + B_2 (C_{2v})$ . The further ordering of the  $A_2$  and  $B_2$  components is now possible using the DICD results. We have already noted that the 500-nm band may be considered as diagnostic of an amine plane perpendicular to the magnetic polarization of the transition at this energy. For these complexes, this plane would be expected to be the ( $xy$ ) plane; this is despite the fact that the ammine groups are not strictly all within this plane, but it has the minimal involvement of the other substituents. Thus this peak may be assigned as having  $z$  polarization for the magnetic transition moment and thus having an overall  $A_2$  symmetry. The higher energy band can then be assigned as  $B_2$ .

## Conclusions

It has been possible to assign from the DICD spectra all the bands arising from the splitting of the parent  $T_{1g}$  band. The overall consistency between the results of the DICD model and the observed DICD spectra support the soundness of the model, suggesting it could prove to be a potent interpretative tool complementary to normal absorption studies in the assignment of d-d transitions.

Another interesting feature to arise from this study is the sensitivity of a particular DICD band to the "chemistry" of the plane perpendicular to the magnetic polarization of the transition responsible for this band. This is dramatically illustrated by the relative constancy of the "amine" band in the DICD spectra (see Figure 5), whereas the band maxima in the normal absorption (Figure 4) manifest no such simple behavior. We have exploited this feature for assignment in this work, but one could envisage its exploitation for monitoring substitution in such a plane for complexes where the DICD spectra have been previously assigned.

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