

A Theory of the Circular Dichroism of the d-d Transitions of Chiral Complexes

Pieter E. Schipper

Contribution from the Department of Theoretical Chemistry, The University of Sydney, Sydney, New South Wales, 2006 Australia. Received May 19, 1977

Abstract: The AICD (associate-induced circular dichroism) model is applied to a consideration of the circular dichroism of the d-d transitions of chiral metal complexes. The unique problems associated with simple static and dynamic coupling models are discussed, and it is shown that purely dipolar terms arising from second-order perturbation theory lead to new mechanisms which are postulated to predominate in leading to the CD activity of d-d transitions. The new mechanisms are conceptually simple, and exploit the low-lying charge transfer states that are characteristic of many metal complexes as intermediate states in the induction process. Detailed selection rules are derived, and the model is applied to a number of series of complexes. Good agreement with experiment is obtained, without the necessity of complex calculations. The model predicts the additivity of the CD of many complexes, and suggests that empirical sector rules for metal complex systems have little theoretical foundation.

Introduction

Circular dichroism has long been recognized as a powerful tool in the study of the stereochemistry of metal complexes and organic compounds. In general, the CD induced in an achiral chromophore by a chiral environment will reflect certain properties of the chirality of the overall molecular structure which, in turn, are a function of the environmental stereochemistry. In this way, direct correlations between structure and CD spectra will exist, so that CD has become a sensitive stereochemical probe. Much of the correlative work in the past, however, has been empirical, but despite the success of empirical sector rules for certain series of compounds, there are sufficient inconsistencies in their use to necessitate a proper theoretical understanding of the mechanisms leading to the CD. Only through a knowledge of the exact mechanisms and consequently the elucidation of the environmental parameters leading to the CD (e.g., should sector rules be adding charges or polarizabilities in the various sectors) can reliable CD/structure correlations be defined.

To elicit the various induction mechanisms, it is necessary to postulate some model for the molecular system. The CD strength of a transition $G \rightarrow E$ (where G designates the ground state of the overall complex and E the excited state at which transition energy the CD appears) may be defined as

$$R_{GE} = \text{Im} (\langle G | \boldsymbol{\mu} | E \rangle \cdot \langle E | \mathbf{m} | G \rangle) \quad (1)$$

where $\boldsymbol{\mu}$ and \mathbf{m} are the electric and magnetic dipole operators for the system as a whole, and may be thought of as the moments interacting directly with the radiation field. The first approach may be referred to as the *complete MO (molecular orbital) model*, and is equivalent to treating the entire complex as a single entity characterized by its molecular wave functions G and E . The CD is calculated directly as matrix elements over these wave functions using eq 1 above, the wave functions being determined by one of the available approximate MO treatments. Such an approach has a number of associated disadvantages. The calculations are time consuming, and often involve a lot of wasted effort in calculating quantities which ultimately cancel in the determination of the final CD. They are not readily transferable from one complex to another, and it is generally difficult to extract physical information from such a calculation about the exact nature of the induction mechanism, unless the basis set has been carefully chosen (which would usually require some preliminary knowledge of the induction mechanism). Such MO methods are best used as a test for or in conjunction with the second approach to be described, or for small systems where a separable chromophore

model is inappropriate. The second approach, and the one adopted in this paper, involves the separation of the molecular system into a finite number of distinct chromophores, and may be referred to as the *separable chromophore model*. Each chromophore is characterized by its free-chromophore wave functions, and there is assumed to be negligible electron overlap between functions on different chromophores. In this way, all electronic integrals over molecule states reduce to matrix elements over the free chromophore functions. This model has been widely used,¹⁻⁶ and overcomes the disadvantages of the complete MO model as the terms responsible for the induced CD may be explicitly derived. The physical interpretation of a particular mechanism is manifest as an interaction between multipole matrix elements on the chromophores with each other and with the radiation field. The model is subject to limitations of application to systems where the exchange terms (electron overlap) between the chromophores are negligible, and we shall see that for most complexes the chromophores may be chosen so that this is indeed the case.

The current separable chromophore models of the CD of achiral chromophores in chiral environments fall into two main categories (the *static coupling (SC)* and *dynamic coupling (DC)* models), and both may be developed using the Rosenfeld equation (eq 1) above.¹ We initially consider the complex or molecule as comprising the achiral chromophore A (with free chromophore states t) coupled via the electrostatic interaction operator V to a single perturbing chromophore B (with free chromophore states u). If G corresponds to the system state where both A and B are in their ground states $t = 0$, $u = 0$, and E to the system state where only A is excited to the state $t = s$, the system states may be expressed in terms of the free chromophore states by using perturbation theory. Defining the product states

$$|tu\rangle = |t\rangle|u\rangle, \quad \langle tu| = \langle t|\langle u| \quad (2)$$

the system states become, to first order in perturbation theory,

$$|E\rangle = |s0\rangle + \sum_{t,u} \frac{V_{AB}(ts,u0)}{(E_s - E_t - E_u)} |tu\rangle \quad (3)$$

with $s = 0$ for G , and

$$V_{AB}(ts,u0) = \langle tu|V|s0\rangle \quad (4)$$

The CD strength for the perturbed $0 \rightarrow s$ transition follows simply from the substitution of G and E , noting that the zero-order term not containing V vanishes (as A is achiral), and retaining only terms that are first order in V . As we shall

only be interested in magnetic dipole allowed transitions (the d-d transitions of metal complexes being electric dipole forbidden in the free ion), the CD strength for a magnetic dipole allowed, electric dipole forbidden transition may be written, to first order in V as in eq 5, where $m_A^0 = \langle s | m_A | 0 \rangle$ and so on. Real wave functions have been assumed, and \mathbf{m}_A , μ_B , etc., are respectively the magnetic and electric dipole operators on the subscripted chromophores. The energies are now transition energies relative to the respective ground states.

$$R_{0s} = -\text{Im} \left[\left\{ \frac{V_{AB}(0t,00)\mu_A^{ts}}{\epsilon_t} + \frac{V_{AB}(ts,00)\mu_A^{0t}}{\epsilon_t - \epsilon_s} \right\} + \frac{2\epsilon_u V_{AB}(0s,0u)\mu_B^{u0}}{\epsilon_u^2 - \epsilon_s^2} \right] \mathbf{m}_A^0 \quad (5)$$

Two types of contributions may be distinguished in the above expression which are directly the basis of the static and dynamic coupling models: (1) those involving only permanent moments on B, so that transition moments are borrowed from A itself due to the mixing of A states by the static field of B (these are the *static coupling* terms, and are those contributions in curly brackets in the above equation); (2) those in which transition moments are borrowed from B, the perturbation acting to link the A and B states (these are the *dynamic coupling* terms, and are given by the last term in eq 5). The two models (SC and DC) are thus complementary in describing the total CD strength in first order.

Higher multipole participation arises through the expansion of V as a multipole series

$$V = V_{dd} + V_{dq} + V_{qq} + \dots \quad (6)$$

where terms involving the charge may be neglected in this two-chromophore case, V_{dd} is the dipole-dipole interaction term, V_{dq} the dipole-quadrupole term, and so on. This expansion is usually fairly rapidly convergent, so that contributions from successively higher multipoles rapidly decrease in magnitude.

The two approaches to the CD of the d-d transitions are based on these static and dynamic coupling models. The static model was first applied to complexes by Moffitt,⁷ and is a natural extension of crystal field theory. The metal ion is postulated as constituting the achiral chromophore, and its free ion states are mixed through perturbations describing the interactions with the ligand environment represented by a crystal-field type expansion (i.e., as a chiral electrostatic charge distribution). This model has been studied more recently by Richardson,^{6,7} who has concluded that it is inadequate in its description of the d-d CD activity because of the unrealistic dependence on the metal-ligand separation. The dynamic coupling model, which involves a dynamic coupling between the metal ion chromophore transition moments and those on the ligand groups, has been postulated by Mason.⁵ In this model, the electrostatic effects of the ligand environment are neglected. This appears to have some agreement with the observed experimental results.

Both these approaches are elegant in their conceptual simplicity, but suffer from a common difficulty which ultimately stems from the high symmetry of the achiral chromophore. In both cases, the achiral chromophore must have an allowed magnetic and at least one allowed electric moment. In general, the d-d transitions are electric dipole forbidden, so that in the case of the DC model, a higher d-d electric transition multipole must participate. For most complexes, the first nonvanishing moment is the hexadecapole, because of the approximate O_h symmetry of the ion. Similar arguments show that analogous electric moments are required for the SC mechanism. The magnetic moment is dipolar in both models, which agrees with the empirical observation that only the magnetic dipole allowed d-d transitions exhibit appreciable CD activity. The underlying

problem in applying these models to d-d transitions may now be clarified in the following way. For increasingly higher symmetry of the achiral chromophore, it is necessary to go to increasingly higher multipole interactions (V_{dh} where h is the hexadecapole moment) before getting a nonzero interaction. We have already seen that such interactions would be much less than, say, the V_{dd} contribution *if it were allowed by symmetry*. However, if we do not restrict the treatment to first-order perturbation theory, it is quite possible that we could get terms quadratic in V_{dd} which, because of the different symmetry requirements resulting from the participation of new intermediate states, do not necessarily vanish and thus could still be appreciably larger than the relatively weak V_{dh} terms arising from first-order perturbation theory. That such contributions in the dipole-dipole approximation are in fact *symmetry allowed* turns out to be the case, and, for reasons that will become apparent later in this paper, they are large for metal complexes because of the characteristic nature of transition metal electronic states.

In this paper, the dipole approximation is retained for both electric and magnetic transition moments, and it is found that, to second order in perturbation theory, purely dipolar terms arise provided that charge transfer states are included in the definition of the achiral chromophore. Some of these terms are of mixed static/dynamic character, and cannot therefore be deduced from purely DC or SC models, even if independently taken to higher order in perturbation theory.

It is not the purpose of this paper to develop the AICD theory in detail, as this has been done elsewhere.⁸ Instead, the applications to polar and nonpolar complexes are discussed, and it is shown that the AICD model provides a unified theory for the CD of the magnetic dipole allowed d-d transitions of a wide range of metal complexes. Furthermore, the results of the AICD model reduce naturally on averaging over all relative orientations of the interacting chromophores to the DICD (dispersion- or dissociate-induced CD) results, which have been shown to give good agreement with experimental results.⁹ It is hoped that this may lead to both a method of assigning the magnetic dipole allowed metal ion transitions (through the detailed selection rules derived herein), and also to the use of d-d CD spectra in reliably predicting stereochemistries of metal complexes.

AICD of the d-d Transitions

Definition of the Chromophores. In discussing the electronic properties of the d-d transitions of metal complexes, there are some important simplifying features which may be exploited in the development of theoretical models. This is particularly so in applying AICD theory, where the definition of the achiral chromophore is crucial to the utility of the model. The states of a typical complex illustrated in Figure 1 (where M is the metal ion, ABCCDD the directly ligating atoms, and XYZ substituted groups or chelate rings) may be partitioned in the following way.

(1) **The d States of the Metal Ion.** These are centered on M, and are assumed symmetry adapted to the crystal or ligand field of the directly ligating atoms ABCCDD. They retain their d character so that transitions between the d states are assumed to be electric dipole forbidden, but some of them will be magnetic dipole allowed. Although there will be some overlap with the states of the directly ligating atoms, any overlap with the ligand substituents XYZ may be safely ignored. Any other free ion states (such as s, p, f states) will be completely neglected.

(2) **The Charge Transfer States.** These will essentially involve the MABCCDD wave functions, and only in exceptional circumstances (e.g., unsaturated chelates) may overlap with less remote ligand substituents. In general, we shall assume negligible overlap with the XYZ states, or absorb substituents

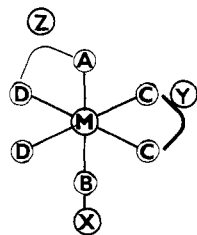


Figure 1. Model of an arbitrary complex of C_1 symmetry, M is the metal ion, ABCDD the directly ligating atoms, X a monodentate substituent, and Y, Z bidentate chelates.

for which this is not the case into the definition of the charge transfer state. The lowest lying charge transfer states, which will be of most importance in the AICD theory, may generally be approximated as a transition from a single ligating atom orbital to a single metal ion d state (or suitable combinations where degeneracies occur) if the charge transfer is ligand to metal, or vice versa if it is metal to ligand.

(3) **The Substituent or In-Ligand States.** These are localized on the ligands proper or on any other substituents. As these provide the chiral perturbation in the AICD model, it is sufficient that only those groups that lead to the chirality of the complex have negligible overlap with the states defined in (1) and (2) above. These states may be localized substituent states, or, in the case of many chelate systems, exciton states of coupled chelate systems. It is important to recognize that the substituent or in-ligand states include the ground state, and the ground state properties of these groups may be replaced by their permanent moments or equivalently their total resultant electric field at the central metal ion. This will become more meaningful anon.

We are now in a position to define the chromophores that are the basis of the AICD model more precisely. The achiral chromophore (which we shall designate by A) may be taken to be that system which gives an adequate description of the states (1) and (2) above, and thus will effectively be the MABCCDD system (see Figure 2). If the metal ion/directly ligating atom system is itself chiral, then this model is not suitable for the calculation of the d-d CD, and it is better to resort to direct MO methods as discussed earlier. The symmetry of the achiral chromophore will thus be that of the MABCCDD system, and must be that of one of the achiral point groups. The d and charge transfer states should therefore transform as the irreducible representations of this point group G_A . In the determination of this point group, it is important to define when ligating atoms are identical. Thus NH_2 , $\text{NH}(\text{CH}_2)\text{HN}$ nitrogens are identical, as chelation will only have a minimal effect on the charge transfer states. In general, chemical intuition should be sufficient to determine whether two ligating atoms are, as far as the d and charge transfer states are concerned, identical. For the example in Figure 2, G_A will be C_{2v} . The remainder of the ligand system constitutes the chiral perturbation, and is subdivided into separate chromophores as best befits the particular ligand system. The total perturbing ligand system (see Figure 2) must have the symmetry of one of the chiral point groups G_C .

It is now possible to develop the AICD model for this type of system. To establish a notation, the d-d transition at which the CD appears will be denoted by $0 \rightarrow s$, where 0 is the ground state and s the excited d state. The charge transfer states of A will be denoted by t , and the transition energies relative to the ground state by ϵ_s , ϵ_t . For the mechanisms that we shall discuss, the perturbing ligand system may be adequately represented by (1) the static electric field \mathbf{E} of the whole ligand system at the metal ion; (2) the excited states u, v (where 0 designates the ground state) of each chromophore B in the ligand system. It will be seen directly that only chromophores with strongly al-

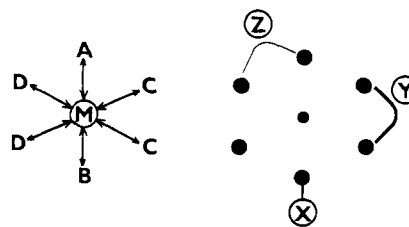


Figure 2. Division of the complex into separate chromophores. The achiral chromophore contains only M and the directly ligating atoms and has C_{2v} symmetry. X, Y, and Z constitute the perturbing chromophore system, which has an overall C_1 symmetry.

lowed electric dipole transition moments from the ground state need be considered.

The AICD of the magnetic dipole allowed $0 \rightarrow s$ transition of A appearing at the transition energy ϵ_s may then be written as eq 7-10 where $\Delta\epsilon_{ts} = \epsilon_t - \epsilon_s$, $\epsilon_{tv} = \epsilon_t + \epsilon_v$, and the interaction operator has the form of eq 11. The μ and \mathbf{m} are the electric and magnetic dipole operators, respectively, on the subscripted chromophore, \mathbf{r}_{AB} is the vector joining the origins of A and B, and the cap denotes the unit vector.

$$R_1^s = \text{Im} \left[\frac{\mu_A^{ts} \cdot \mathbf{E}}{\Delta\epsilon_{ts}} \right] \mu_A^{0t} \cdot \mathbf{m}_A^{s0} \quad (7)$$

$$R_1^d = -\text{Im} \left[\frac{2\epsilon_u V_{AB}(0s, 0u)}{\Delta\epsilon_{us}\epsilon_{us}} \right] \mu_B^{u0} \cdot \mathbf{m}_A^{s0} \quad (8)$$

$$R_2^{s,d} = -\text{Im} \left[\frac{V_{AB}(0t, u0)\mu_A^{ts} \cdot \mathbf{E}}{\Delta\epsilon_{us}\Delta\epsilon_{ts}} \right] \mu_B^{u0} \cdot \mathbf{m}_A^{s0} \quad (9)$$

$$R_2^d = -\text{Im} \left[\frac{V_{AB}(0t, uv)V_{AB}(ts, 0v)}{\Delta\epsilon_{us}(\epsilon_{tv} - \epsilon_s)} \right] \mu_B^{u0} \cdot \mathbf{m}_A^{s0} \quad (10)$$

$$V_{AB} \frac{\mu_A \cdot \mu_B - 3\mu_A \cdot \hat{\mathbf{r}}_{AB}\mu_B \cdot \hat{\mathbf{r}}_{AB}}{r_{AB}^3} \quad (11)$$

The contributions to the CD strength are subscripted by the order of perturbation theory from which they derive, and the superscript denotes whether the contribution is due to static coupling (s), dynamic coupling (d), or a mixture of the two (s,d). The two moments outside the brackets may be thought of as the moments interacting directly with the radiation field, and will be referred to as the field response moments. The other moments are either coupled to each other via the interaction operator V , or to the static field. Note that the field response moments are usually on different chromophores. Thus the electric moment which must come from A in the SC model (and leads to the necessity of using higher multipole moments) is here allowed to be on one of the perturbing chromophores provided that the states of A and B are coupled in some way. The above terms are only the leading terms in the close levels approximation (i.e., those which predominate if $\Delta\epsilon \ll \epsilon$), but will suffice for our applications. Summations over t and u are implied, omitting states with zero energy denominators. Degeneracies are taken to be retained and not split by the chiral interaction, so that the numerators may be summed separately over the components of a degenerate state for a fixed energy denominator.

We must resist the temptation of discussing these contributions in detail at this stage, for a number of them vanish on symmetry grounds, and the remainder may be simplified by similar arguments. These symmetry considerations form the substance of the following section, after which the various mechanisms can be treated in greater depth.

Generalized Selection Rules for AICD

The expressions for AICD have the general form

$$F = \alpha F_A F_C$$

where F_A contains all the matrix elements centered on A, F_C all matrix elements centered on B and the static field, and α all other quantities such as energy and radial denominators. As A is achiral, it must transform according to one of the achiral point groups, G_A . Group theory then restricts the possible combinations of operator and state symmetries that give finite values of the matrix element product F_A . The definition of these symmetry conditions may be referred to as the generalized selection rule for F_A . Consider, for example, the matrix element product arising from R_2^d :

$$\langle 0 | \mu_A | t \rangle \langle t | \mu_A | s \rangle \cdot \langle s | \mathbf{m}_A | 0 \rangle$$

The selection rule is derived in two stages: (1) the *operator selection rule* which defines the polarizations of the dipole operators that are allowed under G_A ; (2) the *state selection rule* which defines the allowed symmetries of s and t for a given ground state symmetry.

The operator selection rules are most restrictive, and are based on the following theorem, which will be discussed in detail in a later paper.

If P^0 is the projection operator for the totally symmetric representation of G_A , and

$$F_A = \sum_{\gamma, \lambda, \dots} \langle a_\gamma^i | P_1 | b_\lambda^j \rangle \langle b_\lambda^j | P_2 | \dots | P_N | a_\gamma^i \rangle$$

$$P^0 \prod_\alpha P_\alpha = \prod_\alpha P'_\alpha$$

then

$$F_A = \sum_{\gamma, \lambda, \dots} \langle a_\gamma^i | P'_1 | b_\lambda^j \rangle \langle b_\lambda^j | P'_2 | \dots | P'_N | a_\gamma^i \rangle \quad (12)$$

The basis functions for A are assumed to be bases for the irreducible representations of G_A , such that b_λ^j transforms as the λ th row of the j th irreducible representation Γ^j . The sum over γ, λ, \dots is over all degeneracies.

The importance of this theorem is that only operator products that are totally symmetric to all operations of G_A lead to finite matrix element products. The operator products then obey the same selection rules as the corresponding macroscopic tensors. The latter have been studied in detail by Birss,¹¹ and the relevant nonvanishing products for the AICD contributions are given in the Appendix in a convenient form using standard chemical notation for most of the common point groups.

The use of these operator selection rules is by no means restricted only to A. If the system C perturbing A also possesses some symmetry, the rules may be applied directly also to F_C . The operator selection rules are generally extremely restrictive, and the definition of the state selection rules is usually trivial once the operator selection rules have been determined; they follow from the usual condition that, for a typical matrix element $\langle b_\lambda^j | P'_\alpha | a_\mu^k \rangle$,

$$\Gamma^j \otimes \Gamma^\alpha \otimes \Gamma^k \subset \Gamma^0$$

where Γ^α is the irreducible representation generated by P'_α , and Γ^0 is the totally symmetric representation of G_A .

These selection rules may now be applied directly to the four contributions of eq 7–10. The first-order mechanisms which lead to the SC and DC models in their simplest form are described by R_1^s and R_1^d , respectively. The static term contains the matrix element product

$$\mu_A^{ts} \mu_A^{0r} \cdot \mathbf{m}_A^{s0}$$

and requires parallel polarization components of the field response moments (which are both on A). The dynamic term requires finite matrix element products of the form

$$\mu_A^{0s} \mathbf{m}_A^{s0}$$

From the tables of the Appendix, it follows that these contri-

butions are restricted to only a small number of achiral point group symmetries (C_{nh} , S_{2n} , C_{3v} , D_{3d} for R_1^s ; C_{nv} , S_4 for R_1^d). As the state selection rules usually add more restrictions, and as most of the achiral chromophores we shall consider have a higher symmetry, we shall not consider these mechanisms further. Note, however, that if we replace one of the electric dipole moments by a higher moment (e.g., hexadecapole under O_h), then these operator products become allowed. This is, of course, the basis of the earlier approaches to d–d CD.

The second-order terms R_2^{sd} and R_2^d contain a common matrix element product of the form

$$\mu_A^{0t} \mu_A^{ts} \mathbf{m}_A^{s0} \quad (13)$$

A cursory glance at the relevant table in the Appendix shows that certain polarization combinations of this operator product are allowed for all point groups, so that these mechanisms will be allowed for any achiral chromophore. In fact, for most symmetries, the operator selection rules require that the three moments in the above product be mutually orthogonal. Although initially this may seem somewhat restrictive, it is actually an extremely significant result, for the state selection rules then restrict the states t that can act as intermediates for a particular $0 \rightarrow s$ transition. Thus a certain magnetic dipole allowed d–d transition will only be CD active if there is a charge transfer state of the appropriate symmetry and sufficient intensity. The state selection rules under these constraints have been tabulated elsewhere, as the same matrix element product appears in DICD theory.⁹

The Second-Order AICD Mechanisms

The use of the separable chromophore model and the particular definition of the various chromophores leads to an explicit separation of the matrix element product on A and that describing the chiral perturbation of the ligand system, allowing us to discuss these factors separately. A further simplification arises from the dependence of both mechanisms on the same matrix element product (eq 13) on A, so that it is possible to discuss the A factor in a general way without recourse to the particular mechanism. The relative importance of the two mechanisms depends exclusively on the particular properties of the ligand system, to which we shall return anon.

The Magnetic Inducibility of A. From the operator selection rules, it follows that the general matrix element product on A (eq 13) is finite only for mutually orthogonal moments. In many cases, it is possible to incorporate this condition into the form of the matrix element product itself, which then becomes

$$\Omega_m(s, t) = \mu_A^{ts} \times \mu_A^{0r} \cdot \mathbf{m}_A^{s0} \quad (14)$$

This quantity also appears in DICD theory,¹² and is referred to as the magnetic inducibility, being the ability of a magnetic dipole allowed transition to have CD induced into it by a chiral perturbation through the particular intermediate state t . The intermediate state must be strongly electric dipole allowed from the ground state, and be relatively close energetically to the d–d transition of interest, a requirement that follows from considerations of the energy denominators. These are precisely the features of charge transfer states in metal complexes, and it is for this reason that it is vital to include such states in the definition of the achiral chromophore. It is also a rationale for the relative inability of higher free-ion states to act as intermediates, as these are generally at considerably higher energies.

As mentioned in the previous section, only charge transfer states of certain symmetry can act as intermediates for a given d–d transition. This may be exploited in the assignment of d–d transitions if the charge transfer states have been assigned, or

vice versa if the d-d transitions have been characterized by some other method.⁹

The magnetic inducibility of A is the same for all complexes with the same metal ion/ligating atom configuration, so that a single computation of this quantity is in principle transferable to a range of complexes. Similarly, the source of the chiral perturbation is conveniently extracted into terms independent of A, allowing for comparative studies of quite different substituent groups.

The Inducing Power. Comparison of the Two Mechanisms.

The two different mechanisms $R_2^{s,d}$ and R_2^d depend on different properties of the chiral ligand system. The matrix element product describing the ligand system may be generally referred to as the *magnetic inducing power* (the ability to induce CD in a magnetic dipole allowed transition). The two different chemical situations corresponding to these mechanisms are summarized in Figure 3.

The $R_2^{s,d}$ mechanism involves a mixed static-dynamic coupling mechanism, and thus cannot arise from purely SC or DC models, even if independently taken to higher order of perturbation. It requires (1) a perturbing group B with a strongly electric dipole allowed transition polarized with components along both the magnetic transition moment on A, and the charge transfer transition dipole; and (2) a strong static field along μ_A^{st} (i.e., perpendicular to the plane of the magnetic and charge transfer moments of A). It is therefore restricted to complexes which are highly polar in character, and it is questionable whether sufficiently strong fields can be set up at the metal ion by the ligand system to make this an effective mechanism.

The R_2^d mechanism is purely dynamic in character, and becomes important if there is a chromophore B with two strongly allowed electric dipole allowed transitions which are not parallel (preferably orthogonal). The matrix element product on B in this case has the form

$$\mu_B^{0u} \mu_B^{uc} \mu_B^{c0}$$

Noting from eq 10 that μ_B^{u0} must have a component along μ_A^{0r} , and that μ_A^{0r} , μ_B^{uc} and μ_A^{cs} , μ_B^{c0} must each have finite dipole-dipole interactions as defined by eq 11, it follows that the inducing power for this mechanism is maximized if

$$\mu_B^{0u} \times \mu_B^{uc} \cdot \mu_B^{c0} \quad (15)$$

is maximized; i.e., the electric moments on B are all strongly electric dipole allowed and mutually orthogonal. In fact, the above product is generally allowed for all chiral point groups, and vanishes for achiral groups, so that it constitutes a general mechanism for any chiral center. The inducing power in this case may be thought of as a purely electric rotational or CD strength, as $\mu \times \mu$ is an axial vector like the magnetic dipole operator, and thus has similar transformation properties. To distinguish this inducing power from that of the $R_2^{s,d}$ mechanism, we shall refer to the expression of eq 15 as the *dynamic inducing power*.

AICD Mechanisms for Metal Complexes

There are two ways of applying the AICD theory to particular systems.

(1) **Quantitatively.** This would involve MO calculations on the achiral chromophore in order to elicit exactly the magnitude and the sign of the matrix element product on A. This magnetic inducibility term also appears in DICD theory, and is thus an important quantity in CD models in general. This is a necessary application, both to establish the theory on a quantitative basis and to elicit the relative importance of the various charge transfer states. This work is in progress, and no attempt will be made to incorporate such work into this paper for a number of reasons. Firstly, in chemical applications, it

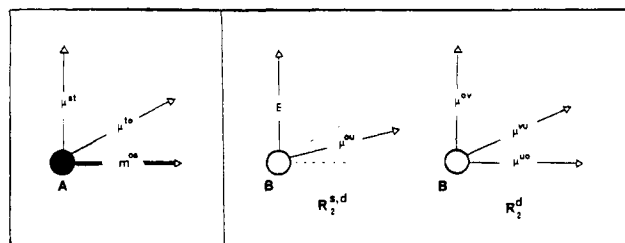


Figure 3. Second-order induction mechanisms. The moments on the achiral chromophore A are mutually orthogonal, and the same for both mechanisms. Orientations of the perturbing moment combinations for the two possible mechanisms are shown for the maximum inductive effect.

is desirable to extract the maximum information without the aid of complex calculations, and this theory is formulated with precisely this aim in mind. Secondly, by comparing the same achiral chromophore in a series of ligand environments, the inducibility is essentially constant, so that the difference in the d-d CD spectra within such a series will be directly attributable to the differences in the ligand environment parameters. This is especially so considering that both second-order mechanisms depend on the same properties (the magnetic inducibility) of A. This then leads directly to the second type of application.

(2) **Semiquantitatively.** In such applications, the effect of the ligand environment only is considered explicitly, and combined with qualitative symmetry arguments for finite magnetic inducibilities of A. We shall see in fact that such applications are sufficiently quantitative to make some sensitive predictions for comparison with experimental data. Furthermore, it is in this form that the theory is without doubt of most value to the chemist, as the ligand parameters in most cases can be interpreted through the basic concepts of charge, polarizability, and dynamic inducing power (which in turn are related directly to simple oscillator strengths), and subsequently used to establish a theoretical basis for the empirically determined sector rules.

In the following applications, two classes of metal complexes will be considered. Typical of nonpolar complexes are the tris (bidentate) complexes in which the chirality of the complex derives from a chiral disposition of the ligands about the metal ion, and not in the chirality of the ligands themselves (the ligands generally being achiral). These are found to have a relatively intense d-d CD,¹³ and can only exploit the R_2^d mechanism in the dipole approximation. The polar complexes we shall consider are the amino acid chelates, in which the chirality does not derive from a chiral disposition of the ligands, but from the intrinsic chirality of the ligand itself. Such complexes are found to have a weaker d-d CD.¹³ Both the $R_2^{s,d}$ and the R_2^d mechanisms could potentially lead to the CD in these cases, but we shall show that the latter leads to a better agreement with the observed experimental results. In both series of compounds, therefore, it would seem that the dynamic inducing power (due to the whole chelate system in the tris chelates, and due to the intrinsic chirality of the separate chelates in the amino acid complexes) of the ligand system is the property leading to the d-d CD, so that it constitutes a new and important parameter in the CD theory of metal complexes.

It is worth at this stage referring briefly back to the precise definition for R_2^d

$$R_2^d = -\text{Im} \left[\frac{V_{AB}(0t, vu) V_{AB}(ts, 0v)}{\Delta \epsilon_{us} (\epsilon_{uv} - \epsilon_s)} \right] \mu_B^{u0} \cdot m_A^{s0} \quad (16)$$

where V is the dipole-dipole interaction operator defined in eq 11. Although the achiral chromophore may be characterized by its magnetic inducibility, and the perturber by its dynamic inducing power, the overall CD (R_2^d) still depends on the *relative orientation* of the moments on B and those on A. Thus

the magnitude of the CD due to a particular perturber **B** will depend on its relative orientation with respect to the achiral chromophore moments. In cases where the achiral chromophore is the same, but there are a number of perturbers **B** in the ligand system, it follows immediately from eq 16 that the total CD of the complex may be written in terms of the contributions $R_2^d(\mathbf{B}_i)$ from the individual perturbers \mathbf{B}_i as

$$R_2^d = \sum_i R_2^d(\mathbf{B}_i) \quad (17)$$

This equation forms the basis of additivity rules for d-d CD, to which we shall return later.

The Dynamic Inducing Power of Tris Chelates. The types of complexes that should exploit the R_2^d mechanism most effectively are those with a number of orthogonal and strongly allowed electric dipole transitions in the ligand environment, leading to a strong dynamic inducing power of the ligand system. Perhaps the best examples are the D_3 tris (bidentate) complexes with ligands such as (phen), (dipy), and (en). These ligands have strongly allowed long axis polarized electric dipole transitions which are skewed in a chiral configuration about the metal ion and couple together to give resultant electric moments which are both strong and orthogonal, leading, as we shall see, to a strong dynamic inducing power. For such complexes, which are generally nonpolar, this is the only second-order AICD mechanism capable of leading to CD of the d-d transitions. Mason¹⁴ has found a correlation between the ligand polarizabilities and the d-d CD, and rationalized this in terms of a dynamic coupling term involving a dipole-hexadecapole interaction. Such a correlation has been found experimentally.¹³ We shall see, however, that this dependence on the ligand polarizabilities is also a feature of the R_2^d mechanism, and it is postulated here that the latter mechanism is responsible for the observed CD.

The chromophores for such complexes may be chosen in the following way. Although the metal ion and the six ligating atoms in an $M(\text{LL})_3$ complex have O_h symmetry, the achiral chromophore is taken to include the metal ion d states and the charge transfer states adapted to S_6 symmetry. This is done as the charge transfer states are found to be sufficiently perturbed by the chelate system to lead to a uniquely defined z axis (along the S_6 rotation axis). The ligand system has effective D_3 symmetry, which is a chiral group as required. The exact model of the ligand system will be defined later.

We can dispense with the achiral chromophore first. Consideration of the state selection rules for A shows that two d-d transitions may become CD active:⁹ (1) the $A_g \rightarrow A_g$ through an intermediate charge transfer state of symmetry E_u ; (2) the $A_g \rightarrow E_g$ through an intermediate charge transfer state of symmetry A_u or E_u . Whether one or both appears depends purely on the energy and intensity of the charge transfer bands.

The effect of the ligand system through its dynamic inducing power may now be estimated by modeling the system in the following way. As the individual ligands have zero inducing power (as they are separately achiral), the states u and v must be states of the coupled ligand system as a whole, and may be developed in terms of the individual ligand states using simple exciton theory.^{14,15} In this way, the dynamic inducing power should be expressible in terms of the properties of the individual ligands and their geometry about the metal ion. Each ligand is characterized by a single excited state r and ground state 0 such that the electric dipole transition moment is long axis polarized. Writing the ligand product functions in the form

$$|000\rangle = |0\rangle_1 |0\rangle_2 |0\rangle_3$$

where 1, 2, 3 indexes the separate ligands, there will be three excited states which represent the symmetry-adapted exciton

functions (chosen to be real for convenience) (eq 18-20). i, j index the two components of v , which is doubly degenerate.

$$|u\rangle = \frac{1}{\sqrt{3}} (|r00\rangle + |0r0\rangle + |00r\rangle) \quad (18)$$

$$|v_i\rangle = \frac{1}{\sqrt{2}} (|r00\rangle - |0r0\rangle) \quad (19)$$

$$|v_j\rangle = \frac{1}{\sqrt{6}} (2|00r\rangle - |r00\rangle - |0r0\rangle) \quad (20)$$

Letting

$$\mu_1^{0r} = \langle 0|\mu_1|r\rangle, \mu_1^{00} = \langle 0|\mu_1|0\rangle, \mu_1^{rr} = \langle r|\mu_1|r\rangle$$

where μ_1 is the intrinsic electric dipole operator of ligand 1, the following matrix elements are readily deduced (eq 21-25). It follows that the inducing power for the whole ligand system summed over the exciton degeneracy reduces to eq 26.

$$\mu^{u0} = \frac{1}{\sqrt{3}} (\mu_1^{r0} + \mu_2^{r0} + \mu_3^{r0}) \quad (21)$$

$$\mu^{0ci} = \frac{1}{\sqrt{2}} (\mu_1^{0r} - \mu_2^{0r}) \quad (22)$$

$$\mu^{0vj} = \frac{1}{\sqrt{6}} (2\mu_3^{0r} - \mu_1^{0r} - \mu_2^{0r}) \quad (23)$$

$$\mu^{v'iu} = \frac{1}{\sqrt{6}} (\mu_1^{rr} - \mu_1^{00} - [\mu_2^{rr} - \mu_2^{00}]) \quad (24)$$

$$\mu^{v'ju} = \frac{1}{3\sqrt{2}} (2[\mu_3^{rr} - \mu_3^{00}] - [\mu_1^{rr} - \mu_1^{00}] - [\mu_2^{rr} - \mu_2^{00}]) \quad (25)$$

$$\frac{3}{2} (\mu_1^{0r} \times [\mu_1^{rr} - \mu_1^{00}]) \cdot (\mu_2^{r0} + \mu_3^{r0}) \quad (26)$$

The magnitude of the above is directly proportional to $|\mu^{0r}|^2$, which in turn is proportional in this one-state ligand model to the polarizability of the individual ligands. The observed dependence of the d-d CD on the polarizability of the ligands in these systems is thus predicted by the R_2^d mechanism.

For the (phen), (dipy), (en) series of a particular metal ion, the magnetic inducibility is essentially constant, so that the d-d CD of $M(\text{phen})_3$, $M(\text{dipy})_3$, and $M(\text{en})_3$ is directly proportional to the inducing powers of the respective ligand systems, and thus the ligand polarizabilities. The relatively large d-d CD for such complexes thus follows directly from their large dynamic inducing powers. The other factor appearing in eq 26 is simply the difference of the permanent dipole moments of the ligand in the excited and ground states, and will be directed along the line joining the metal ion to the center of the respective ligand. The energy splitting of the u and v states has a negligible effect on the CD, and it is possible to put $\epsilon_u = \epsilon_v = \epsilon_r$.

The assignment of absolute configurations of these tris (bidentates) has been attempted by Mason through the CD of the ligand system itself.^{13,14} The u and v states determined above are themselves CD allowed from the ground state, so that two bands of opposite sign appear in the vicinity of the ligand transition energy, but with an energy splitting depending on the degree of coupling of these ligands. The assignment depends on the energy order in which these states appear, so that the energy splitting must be estimated with some degree of accuracy. Unfortunately, this is not a simple task, and it has been suggested that Mason's calculations are not always reliable for assigning absolute configurations on this basis because of the extreme sensitivity of this quantity to the interligand coupling.¹³ The d-d CD, however, has been shown above to be independent of the energy splitting, as the ligand system is essentially seen by the metal ion as an "oriented gas". Thus it would seem that absolute configurations may be more reliably assigned through the d-d CD, as the only quantity depending

Table I^a

Amino acid	$\Delta\epsilon(\text{max})$ [CuL] (i)	$\Delta\epsilon(\text{max})$ [CuL ₂] (ii)	Ratio (ii)/(i)
L-Ala	-0.021	-0.078	3.7
L-Phe	-0.074	-0.255	2.9
L-Trp	-0.152	-1.175	7.2
L-Val	-0.055	-0.260	4.7
L-Pro	+0.193	+0.312	1.6
L-Met	-0.070	-0.202	2.9

^a All data from ref 13 in which original references are collated.

on the absolute configuration is the dynamic inducing power, which in principle may be calculated explicitly and relatively accurately.

The Dynamic Inducing Power of Amino Acid Chelates. We consider now a series of polar metal complexes in which the ligands are intrinsically chiral: the set of bidentate (α -aminocarboxylato)/metal ion complexes, and, in particular, the mono and bis complexes of the Cu(II) ion (Figure 4). The achiral chromophore comprises the d-d transitions of the Cu(II) ion in an approximately D_{4h} environment, and the charge transfer states with the directly ligating atoms. The application of the state selection rules to the achiral chromophore shows that the following d-d transitions are allowed through the bracketed charge transfer states: ${}^2B_{1g} \rightarrow {}^2E_g(E_u, B_{2u})$; ${}^2B_{1g} \rightarrow {}^2B_{2g}(E_u)$. As the bis complexes have twice the number of ligating atoms, we may expect the E_u charge transfer state to be roughly twice the intensity of that of the mono complex, and similarly the magnetic inducibility of the bis should be about twice that of the mono.

The R_2^d mechanism leads to the appearance of CD at both these transitions. The dynamic inducing power of each amino acid ligand is an intrinsic constant of the ligand itself, and it is not possible to estimate this quantity as readily for these ligands without some recourse to their detailed electronic structure. However, we can exploit its transferability as an intrinsic constant of each particular amino acid ligand. It will be a function of the substituted group on the α carbon of the acid, and should not vary dramatically if the substituted groups are similar (e.g., simple alkyl substituents). We can make some deductions about the d-d CD if the R_2^d mechanism is operative in the following way.

The bis trans complexes may be thought of as a simple superposition of two mono complexes, with one rotated through 180° about an axis perpendicular to the chelate plane. As this rotation is a symmetry operation of the bis complex as a whole, the dynamic inducing power of the separate ligands is simply additive. As mentioned above, however, the magnetic inducibility of the bis achiral chromophore is twice that of the mono,

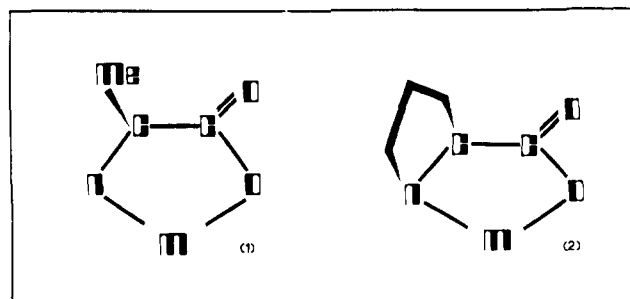


Figure 4. Conformations of the ligands L-alanine and L-proline. Only the α -carbon substituents are assumed to lie outside the plane of the chelate-metal bonds. Hydrogens are not shown.

so that the overall d-d CD of the bis trans complex should be about four times that of the mono if the complex is taken to have an ideal planar geometry. Assuming that the trans predominates in solution,¹⁶ the experimental results¹³ shown in Table I for the ${}^2B_{1g} \rightarrow {}^2E_g$ transition are in remarkably good agreement with the predictions of this model. The results for the ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transition, though not shown, give similar agreement, the d-d CD being about one-tenth and of the opposite sign to that of the 2E_g . The one anomalous result in the table is that proline gives the opposite sign. As proline is unusual in having a ring structure involving the ligated nitrogen, this simply suggests that the dynamic inducing power of the proline ligand is opposite in sign to that of the simpler amino acids—a feature which should transfer to other metal chromophores and other transitions. This is found to be the case.¹³

The Mixed Static/Dynamic Mechanism. The amino acid complexes are polar, and could conceivably induce CD in the d-d transitions through the R_2^d mechanism. The ligand system could then be represented by (1) a static electric field due to the α -carbon substituents, directed perpendicular to the chelate plane; and (2) the π - π^* transition moment of the carbonyl chromophore polarized in the chelate plane along the C=O axis. It is readily shown from eq 9 that this can lead to CD activity of the 2E_g transition of the metal ion, but not the ${}^2B_{1g} \rightarrow {}^2B_{2g}$ (which would require an out-of-plane component of the carbonyl transition moment). As both are observed to be active, this suggests that this mechanism is not responsible for the CD. This is corroborated by the relatively low polarity of the substituents responsible for the electric field, and by the fact that the bis complexes would have eight times the d-d CD of the mono complexes if this mechanism were predominant (twice the number of carbonyl groups, twice the static field, and twice the magnetic inducibility). Thus we may safely assume that the R_2^d mechanism applies to these complexes as well

Table II. Transformation Properties of μm Products

Symmetry groups	Polarizations						
	xx	yy	zz	xy	yx	xz(2)	yz(2)
C_1	xx	yy	zz	xy	yx	xz	yz
C_2	xx	yy	zz	xy	yx	xz	yz
C_{1h}						xz	yz
$C_n (n > 2)$	xx	xx	zz	xy	-xy		
C_{2v}				xy	yx		
$C_{nv} (n > 2)$				xy	-xy		
D_2	xx	yy	zz				
$D_n (n > 2)$	xx	xx	zz				
S_4	xx	-xx		xy	xy		
D_{2d}	xx	-xx					
T, O	xx	xx	xx				
$C_{nh}, D_{nh} (n > 1)$ $S_2, S_6, D_{3d}, T_h, T_d, O_h$							
					None		

Sector Rules

The use of the CD of an achiral chromophore as a tool in the study of the conformation of the molecule as a whole has led to empirical sector rules relating the sign of the CD of the achiral chromophore to the conformation of the rest of the molecule. Such rules have enjoyed much success, especially for organic molecules,¹⁸ and have been stimulated mainly by the octant rule for the carbonyl chromophore. First-order dynamic coupling models employing an electric quadrupole transition moment on the carbonyl chromophore are capable of justifying the octant rule, and thus of giving it a theoretical foundation.

Surprisingly, and perhaps somewhat paradoxically, one of the main reasons for the inadequacy of many of the previous theoretical approaches to the d-d CD problem stems from the assumption that the *empirical* sector rules for d-d CD have a *theoretical* basis; i.e., that the sectors defined in the empirical sector rules must play some role in the interaction mechanism between the achiral chromophore and the ligand system. Such an approach fortuitously works for the carbonyl chromophore, as a relatively low-order moment (quadrupole) is involved.

For d-d CD, an empirical hexadecant sector rule has been postulated,¹³ and works for many complexes. It has therefore stimulated the first-order dynamic coupling approach which under O_h symmetry requires a hexadecapole moment, and thus leads to the hexadecant rule. Unfortunately, exceptions to the rule are sufficient to question its general validity, so that a better approach to the problem (and the one explored in this paper) would seem to be the following: (1) determine all possible induction mechanisms; (2) look at the symmetry or selection rules for the interacting system for each mechanism; and (3) *then* determine the possible conditions when or if these symmetry rules either reduce to the empirical sector rules or are compatible with them. From the results of this work, it would seem that sector rules for complexes are an unnecessary complication, and that it is more important and efficacious to study the geometrical aspects of the relevant induction mechanism directly. Strictly speaking, the R_2^d mechanism suggests that the hexadecant rule is without foundation.

Summary

The applications discussed in this paper suggest that the AICD model, and in particular the R_2^d mechanism, is capable of accounting for the observed properties of the CD of d-d transitions of metal complexes, extracting explicitly the dependence on the chiral part of the perturbing ligand system. Although the applications discussed have been essentially qualitative, the explanations for the relative sign and magnitude for a range of seemingly unrelated complexes is too in-

ternally consistent to be fortuitous. The model is also geared to quantitative studies, and such applications are underway. The latter should establish the R_2^d mechanism as being the predominant method of inducing CD in d-d transitions, and thus provide a unified theory for d-d spectra (both AICD and DICD). It will then be possible to use the theory to make confident predictions of absolute configurations and structure using CD techniques.

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Appendix

The combinations of polarizations that transform as the totally symmetric representations are summarized in Tables II-V. The products $\mu\mu$ and μm transform as second-rank polar and axial tensors, respectively, and $\mu\mu\mu$, $\mu\mu m$ as third-rank polar and axial tensors. The quantity $zzx(3)$ represents the three quantities obtained by permutation of the last coordinate, and so on. Components that are related by symmetry are indicated in the tables. For example, consider the CD strength operator under S_4 ; viz., $\mu \cdot m$. For second-rank axial tensors, yy transforms as $-xx$, xx as xx . Thus $xx-yy$ transforms as the totally symmetric representation, so that the CD strength must vanish (as expected) solely on the basis of the operator selection rules. Another important example is the product $\mu\mu m$ under O_h , whose only totally symmetric components must have the form $\mu \times \mu \cdot m$ as seen from Table V.

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