clopropenium radical $(2/6^{1/2})$[37] is greater than the C1(C3) coefficient in the HOMO of allyl radical $(1/2^{1/2})$. Therefore, the overlap in "model 3,3'-bicyclopropenyl" is over one-third greater than that in "model 1,5-hexadiene".

The long-range interaction between double bonds may be significant in the chemistry of 3,3'-bicyclopropenyl and its simple derivatives. Thus, while the interaction does not significantly stabilize or destabilize the molecule thermodynamically, increased susceptibility to oxidation as well as effects on reactions such as the Cope rearrangement are to be expected.

(37) The degeneracy in cyclopropenium radical is lost when two such "molecular fragments" interact to form "model 3,3'-bicyclopropenyl".

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Interligand Steric Effects in Metal Complexes in Solution Studied through the Residual Circular Dichroism of the d–d Transitions: Application to Tetraaminecobalt(III)–Amino Acid Complexes

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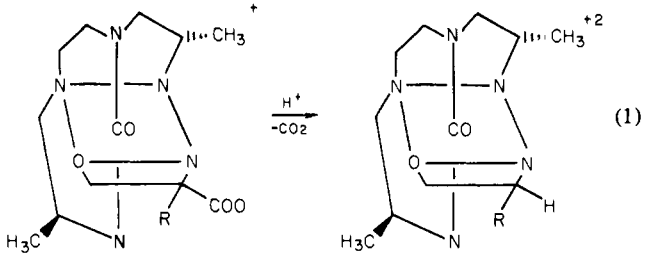
Abstract: Although additivity of d–d circular dichroism (CD) of chiral metal complexes has been demonstrated widely, the deviations from additvity (referred to as the residual CD) may prove paradoxically to be of greater chemical interest. In this paper, the origin of the residual CD is established in its simplest form so that its use in a practical way may be developed. The residual CD is shown to be a sensitive probe for interligand steric effects and the effect of ligand substitution on the metal–ligand bonding. The method is applied to a study of interligand steric effects in a series of tetraaminecobalt(III)–amino acid complexes, leading to a new method for predicting the outcome of asymmetric syntheses carried out on substrates bound to dissymmetric transition-metal moieties.

Introduction

It has been shown previously that decarboxylation of the Λ-β_2 complex **1** in 1 M HCl, to produce bound alanine, leads to a predominance of (*S*)-alanine (eq 1).[2] Examination of molecular



(1)

1

2a, R = H
2b, R = Me
2c, R = Et
2d, R = *i*-Pr

models based on an X-ray crystal structure determination does not reveal any clear difference between (*R*)- and (*S*)-alanine in their steric interactions with the tetraaminecobalt moiety.[3] Furthermore, even if steric interactions could be discerned in the crystal, solvent effects would preclude any positive conclusions as to the steric environment which may exist in solution. We seek a technique which will lead to the elucidation of in-solution steric interactions.

The circular dichroism (CD) of the d–d transitions of the central metal ion constitutes a sensitive probe of the ligand environment. The most common practical use of d–d CD for monitoring stereochemistry has been through empirical sector rules.[4-6] There are extant theoretical works on the subject; however, as discussed in the literature, these rules are generally of limited practical application.[7] There is another set of empirical rules, however, that both is of general applicability and, furthermore, has been shown to have a rigorous theoretical foundation.[8] These are the *additivity rules* which may be illustrated by the following example. Consider a complex, AB_1B_2 (composite complex), with two chiral centers, B_1B_2, and an achiral metal-centered chromophore, A, in which the d–d and charge-transfer transitions are localized. If the complexes AB_1, AB_2 (substitutent complexes) have the same achiral chromophore as the composite complex and B_1, B_2 have the same configurational relationship to A in the composite and substituent complexes, then the d–d CD of the composite complex AB_1B_2 is simply the sum of that of the substituent complexes AB_1, AB_2. This is the simplest example of an additivity rule. Additivity has been addressed empirically and addressed in the models of Mason and Richardson.[9,10]

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Conveniently here, both the conditions for rigorous additivity and the source of deviations therefrom (the nonadditive or *residual* contribution) may explicity be defined in the context of the theoretical model discussed by Schipper.[8] The nonadditive component, more precisely referred to as the *residual CD*, arises from either differences in the substituent and constituent achiral chromophores or differences in the configurational relationship of the chiral groups to A in the constituent and substituent complexes. This is of significant practical importance, because the residual CD may thus be exploited in directly monitoring changes in metal–ligand bonding due to the chiral centers (i.e., changes in the achiral chromophore) or changes in orientation of the substituent groups due to steric interligand interactions in the composite complex which are absent in the substituent complexes.

In this paper, the origin of the residual CD will be established in its simplest possible form, so that its use in a semiempirical and practical way may be developed. The procedure is then illustrated with recourse to a series of complexes to monitor the steric effects which play an important role in the template synthesis of relatively complex organic ligands.

Results and Discussion

Definition of the Residual CD. Consider a metal complex, A_iB_i, in which only one perturbing chiral center, B_i, is present and A_i is the achiral chromophore. (This may, for example, be an asymmetric carbon in the ligand or an asymmetric metal center if the source of the chirality is due to a chiral disposition of achiral ligands about the metal.) It has been shown that the d–d CD of such a system may be described in terms of the AICD (associate-induced CD) model and has the general form[8]

$$R(A_iB_i) = \Omega(A_i)\Lambda(B_i)F_i \tag{2}$$

$\Omega(A_i)$ is the *inducibility* of the achiral chromophore A_i (which effectively encapsulates the metal-ligating atom system) and a function only of the electronic properties of A_i. $\Lambda(B_i)$ is the *inducing power* of the chiral perturber B_i. Both these quantities are defined with respect to coordinate systems fixed to the respective chromophore (intrinsic axes), so that F_i is the orientation factor describing the relative orientation of the A_i and B_i intrinsic systems. Other quantities such as energy and radial denominators are absorbed conveniently into $\Omega(A_i)$ and F_i, respectively. $R(A_iB_i)$ is the d–d CD strength for a specified transition. Detailed interpretation and definition of these quantities may be found in the original reference and deliberately have been omitted from this discussion to avoid detraction from the practical considerations which form the central theme of this paper. In order to simplify the analysis, we have treated effects (by added substituent groups on ligands) originating with changes in the ligand field environment and due to d–d state mixings, changes in d–d state splittings, and reorientations of d–d transition vectors as purely steric effects. At this time, experiments directed at more clearly delineating steric vs. electronic effects are being undertaken.

Suppose now that we have a series of N such complexes, each containing a different chiral center indexed by i ($i = 1, ..., N$). Each such complex may be referred to as a *substituent* complex, with d–d CD having the general form of eq 2.

A *composite* complex is one containing a number of chiral centers. We shall consider initially the most general composite complex $AB_1...B_N$, containing N independent chiral centers. On the basis of the AICD model, the CD of such a complex reduces to the form

$$R(AB_1...B_i...B_N) = \sum_{i=1}^{N}\Omega(A)\Lambda(B_i)F_i \tag{3}$$

The conditions for rigorous additivity, in which the CD of the composite complex is equal to the sum of the corresponding substituent complexes, may be defined by noting that the latter sum has the form

$$\sum_i R(A_iB_i) = \sum_i \Omega(A_i)\Lambda(B_i)F_i^0 \tag{4}$$

The quantities in eq 3 and 4 are strictly equal only if

$$A_i = A \text{ for all } i \tag{5}$$

$$F_i = F_i^0 \text{ for all } i \tag{6}$$

The physical interpretation of these conditions in chemical terms is rather interesting. Condition 5 is equivalent to stating that the achiral chromophore (i.e., the electronic properties of the metal-ligating atom system) is independent of or is not affected by the presence of the chiral centers. For example, the achiral chromophore in the complex A_iB_i must be identical with that in *all* the other substituent complexes. If any chiral center leads to significant changes in the metal–ligand bonding, nonadditivity will result. Condition 6 is equivalent to stating that the orientation of the chiral centers is the same in both the substituent and constituent complexes. This precludes any interactions leading to orientation changes in the chiral substituent groups. For example, any steric interactions between groups B_i, B_j in the composite complex will lead to orientation factors which are different from those in the substituent complexes in which such steric effects are absent. Again this will manifest itself through nonadditivity.

The outcome of these considerations is that nonaddivity of the d–d CD may be exploited directly to study either steric interactions between groups attached to different chiral centers or the effect of a group attached to a chiral center on the metal–ligand bonding. This may be formalized in the following way. Consider the substituent complex A_iB_i with the CD defined by eq 2. If A_i is considered as being a perturbed form of A (for the composite complex), then the inducibility of A_i may be expanded symbolically in terms of that of A:

$$\Omega(A_i) = \Omega(A) + \delta\Omega(A_i) \tag{7}$$

$\delta\Omega(A_i)$ is then the measure of the difference in the achiral chromophore occasioned by removing all the other chiral centers to form the substituent A_iB_i from the composite complex. The exact form of this differential would require detailed considerations of the AICD model (for example, in terms of transition moment and energy differentials), which are outside the scope of this work. The orientation factor may be expanded similarly by the symbolic equation where δf_i is a direct measure of the difference in the

$$F_i = F_i^0 + \delta f_i \tag{8}$$

orientation of group B_i in the two complexes. It follows that the residual CD, ΔR, defined as the observed CD of the composite complex minus the sum of the observed CD of the corresponding substituent complexes, has the form

$$\begin{aligned}\Delta R &= R(AB_1...B_i...B_N) - \sum_i R(A_iB_i) \\ &= \sum_i \delta\Omega(A_i)\Lambda(B_i)F_i^0 + \sum_i \Omega(A)\Lambda(B_i)\delta f_i\end{aligned} \tag{9}$$

where higher order terms have been neglected. This residual CD vanishes for the conditions of rigorous additivity. In practical terms, the complexes should be designed to minimize the number of contributions to ΔR so that, if possible, the residual CD is dominated by a single term.

Fortunately these relationships are not restricted to constituent and pure substituent species. In the more practical situation in which the effect of adding one extra group B_{N+1} on an already composite complex ($AB_1...B_N$) is of interest, it is unnecessary to consider all the substituent complexes.[9] It readily follows from the previous equations that the residual CD for this process monitoring the effect purely of adding B_{N+1} has the form

$$\Delta R = R(AB_1...B_NB_{N+1}) - R(A'B_1...B_N) - R(A_{N+1}B_{N+1}) \tag{10}$$

There is one further feature of the above generalization that is relevant to the applications that follow. Consider the complexes appearing in eq 10. If the actual chromophore is the same for the N and $N + 1$ constituent complexes, then

$$R(AB_{N+1}) = R(AB_1...B_NB_{N+1}) - R(AB_1...B_N) \tag{11}$$

may be interpreted directly as the contribution of B_{N+1} to the CD

of the chromophore A. The significance of this result is that the complex AB_{N+1} may be purely *hypothetical* (i.e., the *real* substituent $A_{N+1}B_{N+1}$ may have a drastically different achiral chromophore leading to large nonadditivity). The relevance of this will be clarified anon.

Isolation of a residual CD correlation with a single steric interaction may be modeled by the substituted (dimethyltrien)cobalt(III)–amino acid complexes, in which both the (*R*)- and (*S*)-amino acid complexes are considered.[11] In the event of maintaining constancy of the achiral chromophore, one may probe for the existence of steric interactions in solution, through the residual CD, in the following way.

(*S*)-am. Consider first the (*S*)-am series. The assumption of negligible steric interactions in this series, together with the observation that the achiral chromophore is insensitive to the secondary carbon substitution would lead to a rigorous additivity of the CD of the form

$$R(AB_cB_a^S) = R(AB_c) + R(AB_a^S)$$

where B_c represents the triethylenetetramine chelate system and B_a^S the (*S*)-aminoacidate ligand. Note that the substituent AB_a^S system is a hypothetical one in the sense discussed earlier (eq 11), as removal of the trien chelate and replacement by, say, NH_3 groups lead to a different achiral chromophore. However, $R(AB_a^S)$ may be interpreted directly as the CD contribution of the B_a^S system to the total CD of the (*S*)-am complex. This is, of course, the quantity of interest, and may be estimated by noting that the AB_c system is experimentally realized by putting $R_a \equiv H$, i.e., the glycinate complex. It follows that

$$R(AB_a^S) = R(AB_cB_a^S) - R(AB_c) = \Omega(A)\Lambda(B_a^S)F(B_a^S) \quad (12)$$

(It is possible that there is some configurational contribution to the CD because of the strict inequivalence of the ligating atoms. However, this contribution is the same for the glycine and the consitituent complex and thus cancels out in the determination of $R(AB_a^S)$; the achiral chromophore may thus be based on equivalent nitrogens.)

(*R*)-am. For the (*R*)-am complex, the contribution to the d–d CD from the amino acid chelate would be exactly the opposite to that in the *S* system for the achiral chromophore based on equivalent nitrogens in the absence of any R_a steric interactions. The inclusion of the latter would lead to a residual CD because of the different orientations of both (or either) R_a and the tetraamine chelate. Thus the residual CD may be defined as eq 13, where ΔR is a measure of the R_a steric interaction.

$$R(AB_a^R) + R(AB_a^S) = \Delta R \quad (13)$$

Residual CD Determination. The $\Lambda(-)_{436}$-β_2-[(dimethyltrien)(aminoacidato)cobalt(III)] complexes were synthesized for both the *R* and *S* forms of the chiral amino acids with R = CH_3, CH_2CH_3, and $CH(CH_3)_2$ (**2b–d**) as the composite complexes $AB_cB_a^{S,R}$. The glycinate (**2a**) was prepared as the substituent complex AB_c. For this initial study, only the case with methyl substituents at the 2,9-positions of the tetraamine was considered. These systems were chosen for two reasons. First, for minimization of steric interactions within the $(dmt)Co^{III}$ moiety, the 2,9 methyl groups should be expected to arrange themselves in such a way that the lowest energy configuration (and hence the principal reaction product in the aminoacidate complex syntheses described in the Experimental Section) would be expected to have both secondary nitrogen atoms in the *R* configuration. This has been confirmed by an X-ray diffraction study.[3] Thus one can be reasonably certain that the configuration at the secondary nitrogen atoms is constant and that differences in the CD between the various amino acid complexes will not be due to gross changes in the tetraamine configuration. Secondly, because of the internal diastereomeric nature of these complexes, they are extremely easily resolved, ensuring high enantiomeric purity. This facilitates the accurate determination of the residual CD.

(11) Abbreviations used: trien ≡ triethylenetetramine; dimethyltrien ≡ (2*S*,9*S*)-2,9-diamino-4,7-diazadecane ≡ dmt; (*S*)-am ≡ (*S*)-amino acid complex, (*R*)-am ≡ (*R*)-amino acid complex; methylalanine ≡ 2-aminobutyric acid.

Table I. Absorbtion Coefficient Ratios for Tetraaminecobalt(III)–Amino Acid Complexes

complex	$\epsilon_{478}/\epsilon_{350}$ for *R*-am	$\epsilon_{478}/\epsilon_{350}$ for *S*-am
2b	0.95	0.98
2c	0.99	0.99
2d	0.96	0.98

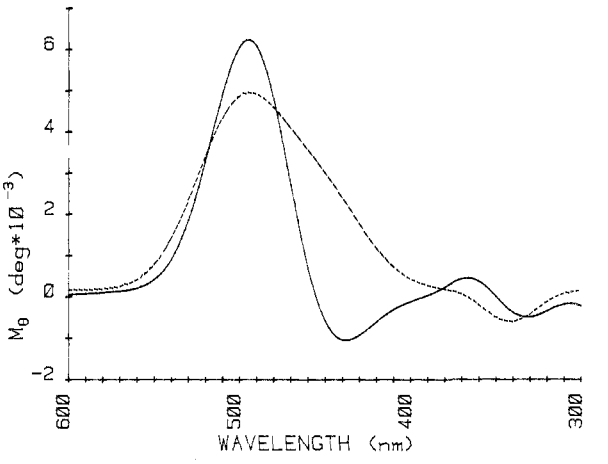

Figure 1. Circular dichroism spectra of $\Lambda(-)_{436}$-β_2-[((2*S*,9*R*)-2,9-diamino-4,7-diazadecane)cobalt(III) (*S*)-methylalaninate]$^{2+}$ (—) and $\Lambda(-)_{436}$-β_2-[((2*S*,9*R*)-2,9-diamino-4,7-diazadecane)cobalt(III) (*R*)-methylalaninate]$^{2+}$ (---) in 1.0 M HCl.

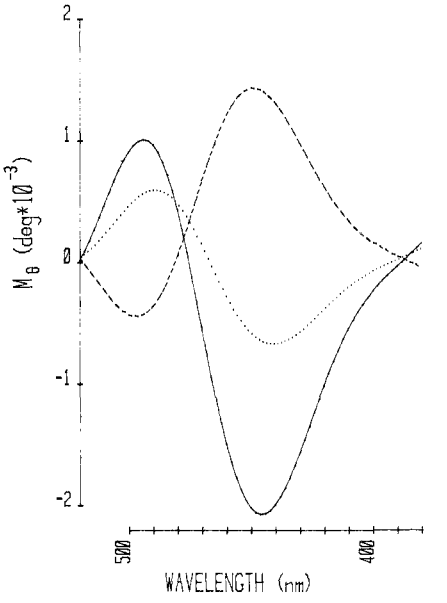

Figure 2. $R(AB_a)$ curves for (*S*)-methylalaninate (—), for (*R*)-methylalaninate (---), and the ΔR curve for the methylalaninate system (···).

The gross stereochemistry of the achiral chromophore in the various complexes (β_1 vs. β_2) is supported upon examination of the normal absorption spectra of the transitions characteristic of the chromophore (d–d and low-lying charge transfer). These results are summarized in Table I which gives the ratio of the absorption coefficients at the two visible bands. This ratio has previoiusly been shown to be sensitive to small changes in the achiral chromophore in that for β_1-(trien)cobalt(III)–amino acid complexes the ratio is greater than 1 and for β_2-(trien)cobalt(III)–amino acid complexes the ratio is less than 1.[12,13] The

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Table II. Residual CD[a] of the Complexes Studied

R_a	$R(AB_a^S)_{tot}$	$R(AB_a^R)_{tot}$	ΔR_{tot}
Me	0.90	0.73	0.16
Et	0.93	−0.57	0.36
i-Pr	0.94	−0.42	0.53

[a] As peak heights in units of $\Delta\epsilon$.

principle CD cotton effects occur between 550 and 400 nm (Figure 1). It is evident that the CD spectrum in the d–d region consists of two dominant peaks.

The $R(AB_a)$'s (vicinal effects)[9] were calculated by subtracting the CD of the glycine complex from the appropriate experimental spectra according to eq 12, as shown in Figure 2 for the (*R*)- and (*S*)-methylalanine complexes. The residual CD's (ΔR) were then obtained from the vicinal effects by application of eq 13, as shown in Figure 2 for the (*R*)- and (*S*)-methylalanine complexes. Similar results are observed for compounds **2b,d** with significant differences between $R(AB_a^R)$ and $R(AB_a^S)$. The $R(AB_a)$ and the ΔR values in Figure 2 are complicated by the presence of two dominant Gaussian peaks. Since it would be extremely difficult to deconvolute these unambiguously, we simply calculate $R(AB)_{tot}$ as the sum of the positive and negative contributions in the 400–500-nm range and ΔR_{tot} as the sum of the ΔR at 445 and 498 nm for comparison. These results are reported in Table II.

Experimental Section

Visible spectra were obtained on a Cary 17 spectrophotometer. CD spectra were obtained on a Cary 61 spectropolarimeter. The pH-stat used in the syntheses is described elsewhere.[14] Cation-exchange resin was Bio Rad AG 50W-X2, 200–400 mesh. Amino acids were purchased from Aldrich Chemical Co. Deconvolution and mathematical manipulation of CD data were carried out with the aid of a Hewlett-Packard 9825 programmable calculator. The previously described amino acid complexes[2] **2a**^{R}, **2b**^{S}, **2b**^{R}, **2d**^{S}, and **2d**^{R} were prepared under controlled conditions, as described below, and crystallized to constant CD, as the perchlorate salts from the major fractions (which were isolated via cation-exchange chromatography in cases where insufficient solubility difference existed to effect rapid purification by crystallization).

$\Lambda(-)_{436}$-β_2-[((2*S*,9*S*)-2,9-diamino-4,7-diazadecane)cobalt(III) (*R*)- or (*S*)-methylalaninate] Diperchlorate (2c). Methylalanine (4.0 mmol) was slurried with $\Lambda(-)_{436}$-α-(dichloro-2,9-diamino-4,7-diazadecane)cobalt(III) chloride[2] (4.0 mmol) in 10 mL of water. The slurry was stirred in a 48 °C water bath while the pH was maintained at 7 ± 0.1 by pH-stat with 1.0 M NaOH. After a few hours the solution had turned orange, and the base addition was complete. The product was precipitated from solution upon addition of excess $NaClO_4$: yield (of (*S*)-amino acid complex) 0.755 g (35%). Anal.: C, H, N.

Conclusion

The earlier assumption that the (*S*)-am complex is relatively free of steric interactions is supported by the slow increase of $R(ABa^S)_{tot}$ as the size of R_a increases. This slow increase is expected simply from the variation of the inducing power and is also found in other amino acid complexes in which steric interactions are absent.[15] The residual CD, however, increases dramatically with the size of the R_a group, indicating a more significant increase in the steric interactions in the (*R*)-am complexes between the R_a and the tetraaminecobalt(III) moiety. Thus the conclusion that the (*R*)-amino acids exhibit greater steric interactions is entirely consistent with the experimental observation that less (*R*)-alanine is formed upon decarboxylation of compound **1**.

This technique has considerable potential in that the amino acid may be used as a probe (manifested through the residual d–d CD) for steric interactions which may exist in solution.

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Reactions Involving Hydrogen Peroxide, Iodine, and Iodate Ion. 7. The Smooth Catalytic Decomposition of Hydrogen Peroxide, Mainly at 50 °C

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Abstract: Substantial progress has been made in the ongoing search for a simple mechanism to describe this complex reaction system over wide concentration ranges. A reasonably good quantitative explanation has been found for the nonoscillatory (smooth catalytic) decomposition of H_2O_2 as it occurred in many early experiments. This explanation rests upon the "skeleton mechanism", which will need further modification to explain induction periods and oscillations. Computer evaluation of the skeleton mechanism proved that the overall rate of the "smooth catalysis" need not be first order with respect to the peroxide concentration even though each peroxide step in the mechanism has that distinction. Free radicals, though undoubtedly present, are not ipso facto involved in the smooth catalysis. In this evaluation, the experimental limiting value, 7.2 min^{-1} at 50 °C, was used as the specific rate for the "electrolytic dissociation" of I_2 into I^+ and I^-.

During the smooth catalytic decomposition ("smooth catalysis") of H_2O_2 in this reaction system,[1-7] the main reaction is

$$H_2O_2 = H_2O + {}^1/_2O_2 \qquad (A)$$

although the approximate proportionality of $[H_2O_2]$ and $[I_2]$[8] gives warning that this equation is deceptively simple. Ultimate simplicity would require $[I_2]$ to be constant, hence independent of $[H_2O_2]$. Nowhere is this true.

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