

Chirality and Bonding in the First Coordination Shells of Three CoN_2Cl_2 Chromophores: Quantitative Reproduction of Rotatory Strengths[†]

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The "d–d" transition energies, absorption intensity distributions, and absolute rotatory strengths and their signs have been quantitatively reproduced for three approximately tetrahedral CoN_2Cl_2 chromophores: dichloro[(-)-sparteine]cobalt(II), dichloro[(-)- α -isosparteine]cobalt(II), and dichloro[(+)- N,N,N',N' -tetramethyl-1,2-propylenediamine]cobalt(II). Reproduction of the signs and absolute magnitudes of the reported circular dichroism spectra has provided a very sensitive probe of the ligand field, represented here within the superpositional cellular ligand-field (CLF) model. The experimental data can be duplicated only with inclusion of ligand-field energy $\{e\}$ and transition-moment $\{t\}$ parametrizations that characterize local misdirected valency. Electron density within the first coordination shells of these complexes is proposed to involve bent, and possibly chiral, bonds in the Co–N regions. These serve to reduce the chirality in the sparteine chromophores from that which might be expected simply from consideration of the twist angle (19 and 6°) between NCoN and ClCoCl planes: it similarly endows the propylenediamine complex with a chirality that is not indicated by the near-mirror symmetry of the first coordination shell.

Introduction

Early in this decade, Mason and co-workers reported rich absorption and circular-dichroism spectra for a short series of nominal tetrahedral CoN_2Cl_2 chromophores. Absorption and rotational strengths were determined from the near-UV region down to 2000 cm^{-1} in the IR region for dichloro[(-)-sparteine]cobalt(II)¹ and dichloro[(-)- α -isosparteine]cobalt(II)² and down to 5000 cm^{-1} for dichloro[(+)- N,N,N',N' -tetramethyl-1,2-propylenediamine]cobalt(II).³ In this paper, we report on the quantitative reproduction of both absorption and rotational strengths for these chromophores right across the experimental energy ranges. Analyses have been performed within our recently developed^{4–6} ligand-field model, the parameters of which sensitively establish a view of bent, and possibly chiral, bonding in the first coordination shells of these complexes.

While ligand-field theory has been employed to model "d–d" transition energies together with associated paramagnetism and electron spin resonance properties for many years, it is only relatively recently that its bona fides within quantum chemistry at large have been firmly established. Its structure and the chemical significance of its parameters have been described formally^{7–10} and in qualitative review.¹¹ Parameters of interelectron repulsion, spin–orbit coupling, and the ligand-field potential proper are energies describing relative shifts of formal d-electron states of the central metal within its environment. Exploitation of the principle of spatial superposition, as in the cellular ligand-field (CLF) model,^{8,11} establishes a division of the ligand-field potential that discriminates between contributions from different ligands interacting with the metal in different symmetry modes; we refer to the energy parameter set $\{e_\lambda\}$, $\lambda = \sigma, \pi_x, \pi_y, \text{ or } \pi_\sigma$, the latter for local misdirected valency as discussed further below. Computations of ligand-field properties beyond transition energies require recognition of the (slight) non-d character of the ligand-field states after the perturbations listed above. For paramagnetic susceptibilities and esr g values, it is sufficient to account for this implicitly within effective magnetic moment operators $kl_\alpha + 2s_\alpha$ ($\alpha = x, y, z$), where Stevens' orbital reduction factor, k , takes values somewhat different from unity.^{7,9,12} The calculation of spectral absorbance, however, begets a more extensive, and chemically revealing, parametrization scheme.

In outline, our recent development^{4–6} of the ligand-field scheme to service "d–d" spectral intensities considers ligand-field orbitals resulting from the energy perturbations above as combinations of d orbitals with local, or cellular, bond orbitals. By this means, the model incorporates the same spatial superpositional structure of the prior energy scheme and its parameters ultimately refer to local σ and π bonding. The approach addresses electric-dipole components of transition moments and, recalling the selection rule

$\Delta l = \pm 1$, focuses especially upon those parts of the non-d admixtures in the cellular ligand-field orbitals that are of p or f character when referred to the metal atom as origin. Writing

$$\psi_\lambda = d_\lambda + b\phi_\lambda \quad (1)$$

for a ligand-field orbital of λ symmetry referred to the local cellular environment, we consider the electric-dipole transition moments $\langle \psi_\lambda | e z | \psi_\lambda \rangle$ in order to define the model parameters:

$$\begin{aligned} \langle \psi_\lambda | e z | \psi_\lambda \rangle &= \langle d_\lambda | e z | d_\lambda \rangle && \text{I} \\ &+ b_\lambda [\langle d_\lambda | e z | \phi_\lambda \rangle + \langle \phi_\lambda | e z | d_\lambda \rangle] && \text{II} \\ &+ b_\lambda^2 \langle \phi_\lambda | e z | \phi_\lambda \rangle && \text{III} \end{aligned} \quad (2)$$

Terms I vanish identically, and terms II survive only for those parts of ϕ_λ that transform as p_λ or f_λ referred to the metal as origin. We refer to the variables ${}^L t_\lambda$ ($L = P, F$) accordingly:

$${}^P t_\lambda = b'_\lambda \langle d_\lambda | e z | p_\lambda \rangle \quad (3)$$

$${}^F t_\lambda = b''_\lambda \langle d_\lambda | e z | f_\lambda \rangle \quad (4)$$

in which b' and b'' subsume all mixing coefficients deriving from the ligand-field orbitals (1) and from the expansions of ϕ_λ as multipoles centered on the metal. Term III is defined as ${}^R t_\lambda$ and has been shown⁶ to make possibly intrinsically significant contributions that ultimately, however, cancel in chromophores with global bipyramidal or antiprismatic symmetries.

Overall, therefore, the ligand-field model we employ is characterized by two formally independent parameterization schemes—one, $\{e\}$, for energies and one, $\{t\}$, for intensities (or electric-dipole transition moments). However, interpretations of actual parameter values for each set are made by reference to the

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[†] No reprints available from this laboratory.

same chemical bonding concepts applied to the same environments and electron density distribution. In recent papers,^{5,6,13-15} we have begun to establish both empirical and theoretical correlations that provide a unified modeling and comprehensibility of both energy and intensity aspects of "d-d" transitions. Full details and formalism of the intensity model as applied to acentric chromophores acquiring intensity from the static features of the coordination have been published.⁴⁻⁶ Extension to centrosymmetric chromophores and the case of vibronically allowed transitions arising from the dynamic character of the metal environment has been completed, and a report is in preparation.

Armed with working parametrizations of both ligand-field energies and electric-dipole transition moments, computations of natural circular dichroism (CD) follow directly. Apart from the single orbital reduction factor of the magnetic moment operators, no further variables or assumptions are required for this extension. In short, a successful account for "d-d" absorption intensities should simultaneously furnish quantitative reproduction of the associated "d-d" CD spectrum. The present study addresses this prospect. The successful outcome illustrates how the CD experiment sensitively establishes a detailed view of the ligand field and of the chemical bonding which that probes.

The Context of the Ligand-Field Model

The position of the present ligand-field model for spectral absorbances and rotational strengths is now briefly reviewed within the long history of chiroptical theory. An important and detailed review of other approaches has been made by Richardson.¹⁶

The rotatory strength, R_{ij} of an electronic transition between molecular states Ψ_i and Ψ_j is given by Rosenfeld's¹⁷ expression

$$R_{ij} = \text{Im} \langle \Psi_i | \hat{\mu} | \Psi_j \rangle \cdot \langle \Psi_j | \hat{m} | \Psi_i \rangle \quad (5)$$

where $\hat{\mu}$ and \hat{m} are the electric- and magnetic-dipole operators, respectively. Different models entertained for the computation of rotational strengths over the years have arisen from the necessity of constructing various approximate descriptions of the states $\{\Psi\}$. Some of the earliest of these involved molecular orbital descriptions of the simplest kind, even when quite detailed consideration was occasionally given to the minutiae of coordination and bonding. Within the transition-metal area, one thinks of Liehr's¹⁸ modeling of "misdirected valency", for example. Numerical application of Liehr's approach by Piper and Karipedes,¹⁹ however, proved quite inadequate to reproduce the observed spectral chirality in [Cu(en)₃]³⁺. In fact, the use of approximate molecular orbital models was generally disappointing at that time: the same was true for similarly based computations of ligand-field energies.

By far the most widely exploited and successful modeling of both spectral absorbance and chirality has been that founded on the so-called "independent systems" approach. This highlights a natural focus upon the separation of chromophoric center, associated with which are the observed spectral transitions of interest, and the associated moieties—the perturbers—through which the system acquires dipole and perhaps chiral strength. One considers product functions between members of a chromophore set, $\{A\}$, and perturber set, $\{B\}$, which are deemed to interact through an electrostatic operator, V , that neglects exchange. The neglect is accomplished by a presumption of vanishing overlap between the A and B subsystems that begets the qualifier "independent" in the name of the scheme. Interactions between the subsystems are framed within a perturbational approach and are subdivided into so-called "static" and "dynamic" contributions. The former define matrix elements of the kind $\langle A_i B_0 | V | A_j B_0 \rangle$ and are closely linked to the traditional crystal-field perturbation in the context of transition-metal complexes. The latter refer to elements of the

kind $\langle A_i B_0 | V | A_j B_k \rangle$ and, because these imply consideration of virtual excitations on the perturber B group, also define the notion of the "coupled oscillator".

Celebrated studies of the static coupling are those of Judd²⁰ and of Ofelt²¹ for the absorbances in lanthanide "f-f" transitions. Electric-dipole intensity is Laporte-forbidden for pure f-f transitions, of course. The required parity mixing that enables these transitions was expressed within what would now be called the "static coupling" framework by consideration of configurational mixing between the ground f^n states and those from excited $f^{n-1}d^1$ and $f^{n-1}g$ configurations of the metal brought about by interaction between the metal and ligand subsystems. An intermediate step and important formalism in these studies was the construction of operator equivalents such that matrix elements of the form $\langle f^n | \hat{\mu} | f^n \rangle$, where the quotes signify the mixed parity of the "real" functions, are equivalenced by matrix elements of the kind $\langle f^n | \hat{T} | f^n \rangle$, where T is an effective, even-parity operator. The T operator is expanded as a multipole series so that the power of the Wigner-Eckardt theorem and of tensor operator theory in general may be fully exploited. Good reproduction of experimental absorbances was achieved by Judd,²⁰ except for the so-called "hypersensitive" transitions. These were shown²⁰ to be associated with the second-order terms $T^{(2)}$ of the effective tensor operator. Later studies by Jørgenson and Judd,²² Mason et al.,²³ and Judd²⁴ included terminology like "the dynamic coupling with the inhomogeneous dielectric of the environment" but were able to give satisfactory accounts of the hypersensitive transitions in terms of what is now recognized as the "dynamic coupling" terms outlined above. Richardson's review¹⁶ of the independent systems scheme appeared at that time.

Since then, Richardson and his colleagues²⁵⁻²⁸ have developed and tested the approach, mostly within the f block, in great detail. They have been particularly concerned to investigate the relative roles of the static and dynamic coupling (SC and DC) contributions in real systems. Like Judd,²⁰ they have first constructed effective, even-parity, transition-moment operators and sought to fit the multipole coefficients empirically to experiment. Then, in an essentially separate procedure, they have attempted to model those phenomenological coefficients in terms of SC and DC contributions: these were estimated from consideration of the basis A and B subsystems with regard to the mean n th power radii of the metal f orbitals and the mean and anisotropic polarizabilities of the B group species, comprising both ligands and bond densities. Fair success at a semiquantitative level has been achieved. The studies have demonstrated the great importance of the DC contribution as well as the SC contribution, and overall, they have built confidence in the broad concepts of the independent systems approach.

The order of perturbation to be employed within this scheme has excited some comment by Schipper.²⁹ Introducing the abbreviated notation¹⁶

$$R_{0m} = \text{Im} \langle A_0 B_0 | \hat{\mu} | A_m B_0 \rangle \cdot \langle A_m B_0 | \hat{m} | A_0 M_0 \rangle \\ = \text{Im}(P_{0m} \cdot M_{m0}) \quad (6)$$

for the rotatory strength of an electronic transition between metal functions, $0 \rightarrow m$, one may expand R_{0m} to second order in V :

$$R_{0m} = R_{0m}^{(0)} + R_{0m}^{(1)} + R_{0m}^{(2)} \quad (7)$$

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where

$$R_{0m}^{(0)} = \text{Im}(P_{0m}^{(0)} \cdot M_{m0}^{(0)})$$

$$R_{0m}^{(1)} = \text{Im}(P_{0m}^{(0)} \cdot M_{m0}^{(1)} + P_{0m}^{(1)} \cdot M_{m0}^{(0)})$$

$$R_{0m}^{(2)} = \text{Im}(P_{0m}^{(0)} \cdot M_{m0}^{(2)} + P_{0m}^{(1)} \cdot M_{m0}^{(1)} + P_{0m}^{(2)} \cdot M_{m0}^{(0)}) \quad (8)$$

where superscripts refer to zero-, first-, and second-order contributions. In transition-metal complexes, where the A (=M) subset spans pure metal functions, both $P_{0m}^{(0)}$ and $R_{0m}^{(0)}$ vanish for pure d-d transitions, so that one considers only

$$R_{0m} = R_{0m}^{(1)} + R_{0m}^{(2)} = \text{Im}(P_{0m}^{(1)} \cdot M_{m0}^{(0)} + P_{0m}^{(1)} \cdot M_{m0}^{(1)} + P_{0m}^{(2)} \cdot M_{m0}^{(0)}) \quad (9)$$

As zero-order magnetic dipole elements do not vanish for d-d transitions, it is common to neglect the second term in (9). Further, most calculations have also neglected the third term, assuming the second-order electric-dipole elements to be much smaller than those of first order. However, Schipper²⁹ has pointed out that electric quadrupolar moments and higher are required within the $P^{(1)}$ expansion but only dipole and higher in $P^{(2)}$ and on these grounds argues that the oft-neglected third term in (9) will actually be dominant.

More recently, Schipper and Rodger³⁰ have examined the structure of the independent systems approach in some detail. They were especially concerned to see how it is that some applications of the static coupling model have met with fair success while, in others, dynamic coupling terms become important or even predominant and to see why Schipper's second-order model may be most appropriate in yet other situations. They provide a formal analysis of the independent systems approach in which the efficacy of these various models or "mechanisms" present themselves as different components of the perturbation expansion. In particular, Schipper and Rodger show how the symmetry of the achiral chromophore is of especial significance in the determination of which perturbation and multiple contributions will dominate in any particular study. In so doing, they have provided an overview of the independent systems model that brings a cohesion to that whole approach.

This very brief summary of the independent systems method as applied to most groups since the mid 1970s is, of course, cursory in the extreme. It is not intended to be dismissive in any way but merely to provide a point of departure for a discussion of the place of our ligand-field model in this long-researched area. In doing so, it is worth noting that the independent systems scheme, as developed, has some power of generality in that the subsystems, A and B, need not refer to a transition-metal and ligand set. Höhn and Weigang,³¹ for example, exploited the formalism in a study of the optical activity in organic systems in which nearby π moieties endow a σ -bonded chromophoric center with rotational strength. The wide potential of the approach must be expected to carry with it the usual penalties of occasionally not providing an ideal starting point for any one application. While this may not be too serious an objection within a parametrized approach—as the above eventually is—it is relevant in discussions of the order of perturbation ultimately required to yield a good interpretation of the multipole parameters.

By contrast, ligand-field theory is not general at all, being applicable strictly within the "ligand-field regime". One considers matrix elements of various effective operators within a pure d (or f, for lanthanides) basis. As described fully and at various levels of formality elsewhere,⁷⁻¹¹ the d (or f) functions have radial character determined by and for the object molecule as a whole. Ligand-field theory is to be seen as a projection of the many-electron molecular problem onto this "mean d (f) orbital" basis. The complementary subspace of "rest" functions (i.e. the rest) interact with the d (f) electrons and one recognizes the dominance

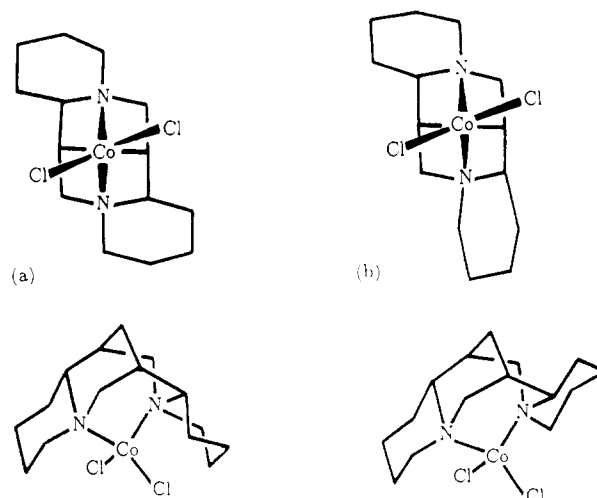


Figure 1. Coordination geometries of (a) dichloro[(-)- α -isosparteine]cobalt(II) and (b) dichloro[(-)-sparteine]cobalt(II).

in that "rest" set of the bonding electron density throughout the molecule. The influence of these complementary functions are left implicit within ligand-field theory, however, being "folded into" the effective operators that are ultimately parametrized. The computation of electric-dipole transition moments within our ligand-field model⁴⁻⁶ involves empirical fitting of the coefficients of the multipole expansion of effective transition-moment operators. At that stage, there is a direct one-to-one mapping with the end result of the first stage of Judd's or Richardson's procedures. In either approach, the p or f character that endows "d-d" transitions with their intensity is parametrized by these effective operator expansion coefficients. Our approach differs in the manner, though not ultimately in the physical basis, of interpretation of these empirical parameters. While Richardson models them quantitatively through estimation of metal f (or, in principle, d) radial character together with ligand and bond polarizabilities, we limit ourselves to a qualitative assessment centered upon a simple molecular orbital approach. That was the basis of our introductory review of the $\{t\}$ parameters above. It is important to emphasize, however, that the process of relating the t parameters to the multipole coefficients of the effective T transition-moment operator, does not depend upon the modeling or interpretation of the t parameters themselves. In using the simple molecular orbital description of the cellular ligand-field orbitals in (1) as a basis for interpretations, we do not expect to suffer the extreme difficulties of the earlier molecular orbital treatments of absorption and rotatory strengths. This is not just because our interpretations are qualitative and hence not subjected to the discipline of numerical computation. Rather, it is because of the central and well-attested idea in ligand-field analysis of the division between "mean d orbitals" and "the rest". Thus, the process of complex formation, involving all charge redistribution associated with bonding, is implicitly taken account of in the ligand-field projection. The "dynamic coupling" terms of the independent systems approach may be seen as recognizing the polarization of ligand functions on complexation. Within our scheme, that polarization is probed through the differing ratios of $P_{t\lambda}^d : F_{t\lambda}^d$ in any given complex. In resisting any quantitative modeling of the $L_{t\lambda}$ parameters within our scheme, we adhere to a philosophy that ligand-field theory be excused the tasks of bonding theory.³² It is the case, after all, that computations of state energies and properties of transition-metal complexes at the level of accuracy probed by d- or f-electron spectroscopy and magnetism are generally beyond contemporary computing power. Our ligand-field approach seeks to separate that which is calculable within reasonable approximation—essentially the angular quantities—from those which are not and then to correlate the latter with broad-based chemical concepts as best we might.

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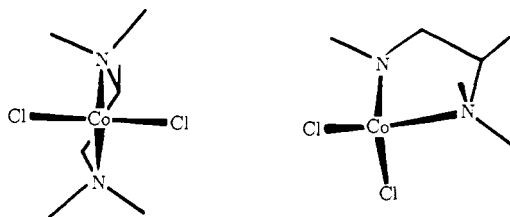


Figure 2. Coordination geometry of dichloro[(+)-*N,N,N',N'*-tetramethyl-1,2-propylenediamine]cobalt(II).

Geometry and Computational Basis

The coordination geometries of the sparteine³³ and isosparteine³⁴ complexes are illustrated in Figure 1. In each molecule, chirality might be presumed to arise from the loss of mirror planes in the nominal tetrahedron following rotations of the ClCoCl planes with respect to the NCoN planes caused by steric interactions of the chlorine atoms with the bulky sparteine ligands. These rotations have been determined as ca. 19° in the isosparteine molecule and ca. 6° in the sparteine. A more subtle origin of chirality must be proposed for the propylenediamine complex³⁵ for, as shown in Figure 2, the disposition of the donor atoms about the metal closely approximates C_{2v} symmetry.

Calculations of transition energies, absorption intensity distributions, and CD within the ligand-field approach was implemented within the CAMMAG3 program suite³⁶ developed in this laboratory. Relationships between the different parts of the calculation are sketched in Figure 3. In the first stage, the matrix of given free-ion states—chosen as $^4F + ^4P$ in the present study—is numerically diagonalized under the ligand-field Hamiltonian,⁹ \mathcal{H}_{LF}

$$\mathcal{H}_{\text{LF}} = \sum_{i < j} U(i, j) + \zeta \sum_i l_i \cdot s_i + \sum_i V_{\text{LF}}(r_i) \quad (10)$$

in terms of energy parameters referring to interelectron repulsion (Racah), spin-orbit coupling (ζ), and the cellular ligand-field potential (e_λ). Differences between the resulting eigenvalues are then matched to experimental transition energies by iterative variation of the system parameters. Eigenvalues together with their associated eigenvectors, optimized in this way, are then held fixed for the computation of derived ligand-field properties. For “d-d” spectral absorbance, the $\{^4t_\lambda\}$ parameters of the local transition moments are varied for optimal reproduction of intensity distribution. Then, if desired as here, a simultaneous computation of rotatory strengths for comparison with the (solution) CD experiment is undertaken by forming the scalar products of the electric-dipole transition moments, parametrized with the t variables as above, and the magnetic dipole moments, parametrized with k , as described, for example, by Schellman.³⁷ The whole analytical process is thus one of optimizing values for two sets of parameters (plus k)—the $\{e_\lambda\}$ for eigenvalues, and the $\{^4t_\lambda\}$ for eigenvectors. Most usually we iterate the t parameters separately from, and subsequently to, the optimization of the e set. However, they may be iterated together, and indeed a significant part of the present analysis was conducted in this way.

Analyses and Discussion

A. Dichloro(−)- α -isosparteine]cobalt(II) and Dichloro(−)-sparteine]cobalt(II). Analyses for these two closely related chromophores followed closely similar but independent paths. Except where explicit mention is made, all descriptions in this section apply equally to the two systems. The analyses began with the obvious and usual assumption that the ligand field is defined by the location of the donor atoms about the central metal ion. In addition to the Racah B parameter for interelectron repulsion and the spin-orbit coupling coefficient, ζ , we included the CLF

parameter set: $e_\sigma(\text{N})$ for the sparteine amine ligands and $e_\sigma(\text{Cl})$ and $e_\pi(\text{Cl})$ for the halogens. Variation of this small parameter set readily yielded quantitative reproduction of the observed “d-d” transition energies with essentially unique parameter sets for each chromophore.

Parametrization of the intensity distributions began with variation of $^4t_\sigma(\text{N})$, $^4t_\sigma(\text{Cl})$, and $^4t_\pi(\text{Cl})$; $L = P, F$. Again, quantitative reproduction of the five regions or bands, shown in Figure 5, was achieved for each chromophore but for several discrete sets of t values. This ambiguity undoubtedly arises from the number of t parameters being one greater than the number of observed bands, although we have found in other intensity analyses^{5,13} that implicit constraints (determined essentially by the fixed chromophore geometry built into the calculation) often permit unique solutions even when there are apparently less observables than parameters.

Concurrent with these computations of absorption intensity distributions, we calculated rotatory strengths for comparison with Drake et al.’s CD spectra.^{1,2} Only one more parameter is involved here: namely, the orbital reduction factor, k , in the magnetic moment operators, $\mu_\alpha = k l_\alpha + 2s_\alpha$ ($\alpha = x, y, z$). Contributions to calculated rotatory strengths from the spin angular momentum only arise through spin-orbit coupling effects so that we observe calculated CD as very nearly proportional to k . Although no approximations are made in this respect within our calculations, discussions can be made to good accuracy in terms of k acting simply as a scaling factor for calculated rotatory strengths. For each of the t parameter sets affording good reproduction of the absorption spectra, we found, for both of the present chromophores, broadly satisfactory reproduction of the signs of observed rotatory strengths, but their calculated magnitudes were 10–12 times greater than experiment, when $k = 1.0$. While the average magnitudes of the rotatory strengths could be brought into correspondence with experiment by reducing k to 0.1 or less, we consider such a tactic unphysical and unacceptable. In any case, the *detailed* magnitudes of individual CD features are still not very well reproduced.

Thus far, only P - and F -type intensity parameters had been included in the analysis. Contributions from R -type parameters are identically zero within a tetrahedral chromophore as demonstrated theoretically elsewhere,⁶ and experience,^{6,13–15} to date suggests that their effects in near-tetrahedral symmetry are negligible. Nevertheless, we performed calculations at this stage with inclusion of non-zero $R^t_\sigma(\text{N})$, $R^t_\sigma(\text{Cl})$, and $R^t_\pi(\text{Cl})$ parameters. As expected, only very small changes in either absorption or rotatory strengths were calculated in this way. Following this check, R -type parameters were neglected in the remaining investigation.

So, for each chromophore independently, no satisfactory account of the spectral chirality could be made simply in terms of the ligand donor atoms and associated parameters described so far. We therefore considered the coordination geometry in more detail. In Figure 4 are shown two approximately orthogonal views of the α -sparteine molecule: similar sketches serve for the sparteine chromophore also. A major departure from T_d coordination geometry in addition to the aforementioned rotation of the ClCoCl plane to reduce steric interaction with the sparteine, as indicated, is the small N-Co-N angle (ca. 90°) forced by the chelation. We suppose that, in regions close to the metal atom, interelectron repulsions are minimized with a tetrahedral disposition of electron density. (As discussed elsewhere,^{9–11} we envisage the bonding electrons to derive primarily from the metal s and/or p valence shell, with d electrons playing only a minor role.) In regions between the metal and each donor nitrogen, compromises are made and bent bonding results.

The consequences of such misdirected valency for ligand-field analysis have been studied in some detail by us, both with respect to the energy, e , parametrization^{38–41} and to the intensity, t ,

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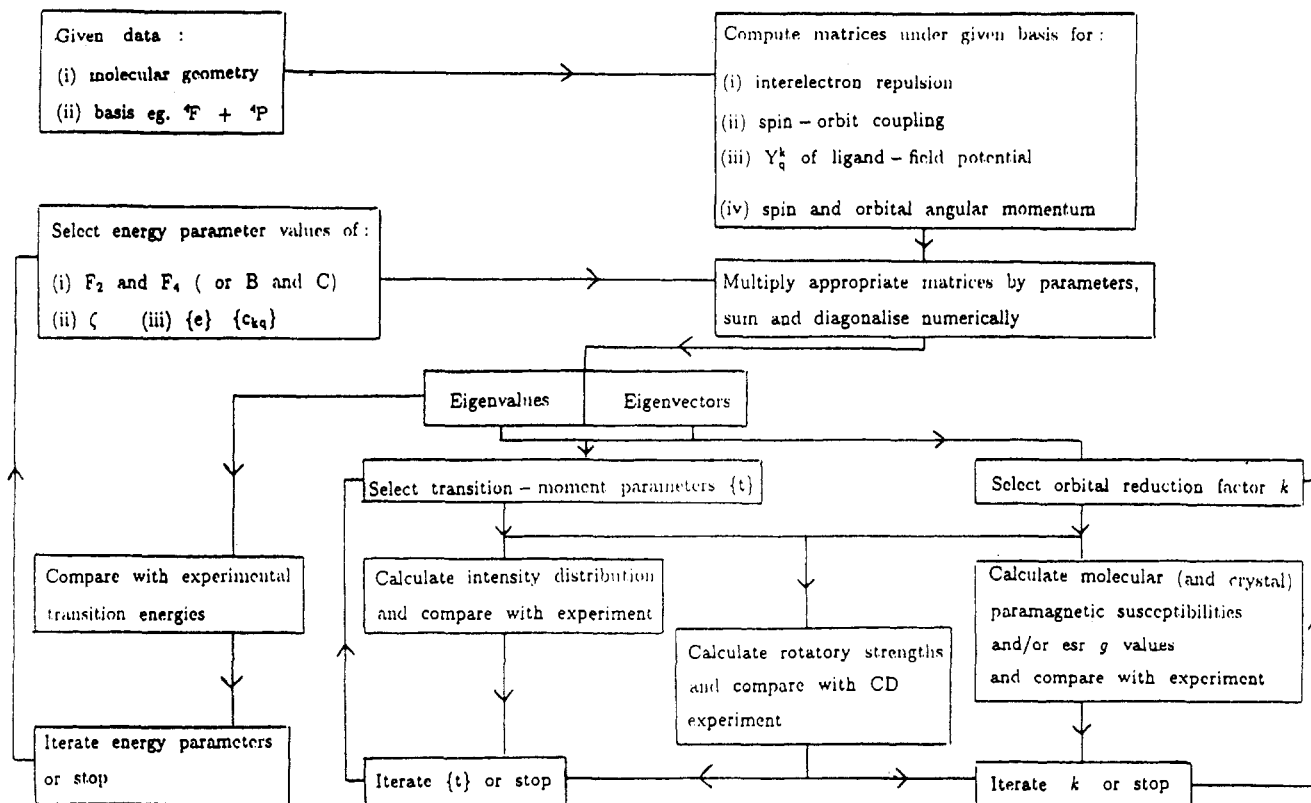


Figure 3. Schematic block diagram of the computation of transition energies, absorbances, and circular dichroism showing iteration routes for e and t (and k) parameters.

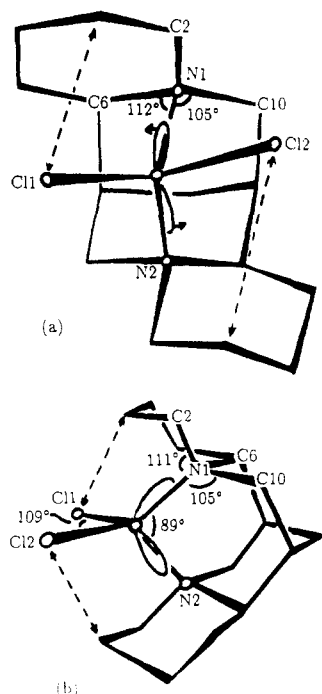


Figure 4. Proposed bent bonding in the isosparteine complex. That for the sparteine chromophore is similar.

parametrization.¹⁵ For the interaction Co-N1, for example, we choose z parallel to Co-N1 and y perpendicular to the plane defined by Co, N1, and C2. For the misdirected valency, the local e parameter set is augmented with $e_{\pi x}$ and the off-diagonal variable $e_{\pi\sigma}(xz)$, and the t parameter set with $t_{\pi x}$ (even for, as here, ligands considered as pure " σ " donors). With these extra contributions included (similar for Co-N2), energy, intensity, and CD analyses

for each sparteine chromophore were begun afresh. Calculations were performed with $e_{\pi x}$ and $e_{\pi\sigma}(xz)$ values in the range -2000 to $+2000$ cm^{-1} and for $t_{\pi x}$ values free. With appropriate variation of all other parameters, we were able to reproduce both observed transition energies and relative absorption intensities, once more, but *not* the detailed relative or absolute magnitudes of the CD rotatory strengths. We therefore considered the detailed chromophore geometries once again.

We argue above that the primal cause of the proposed bent bonding for the Co-N interactions is the tendency for the bonding electron density close to the metal atom to assume a tetrahedral disposition. In the absence of contrary forces, the bonds themselves will similarly take up that arrangement: we note the Cl-Co-Cl angles in these chromophores are very close to 109° . In addition to the bent bonding in local Co-N xz planes, described above and caused by the chelate ring formation, we expect some rotation of these bonds in the sense indicated in Figure 4a following the rotation of the ClCoCl plane. That these Co-N bonds are expected to rotate somewhat *with* the ClCoCl plane immediately offers hope of success in the CD calculation, for it implies a diminished degree of chirality with respect to that which might be expected (and so far built into the calculations) simply by reference to the donor atom coordinates. In further support of the proposed location of the Co-N bond density, we note the smaller CoNIC10 angle (105°) relative to either CoNIC6 (112°) or CoNIC2 (111°), suggesting that a tetrahedrally disposed nitrogen donor orbital is oriented into the same region of space. The idea was tested within the ligand-field model simply by inclusion of e_x and $e_{\pi\sigma}$ parameters for the local C-N yz planes, together with intensity parameters, t_{xy} . After wide variation of this extended parameter set, we were able to reproduce, *quantitatively*, all experimental data—transition energies, absorption intensity distributions, and the signs and magnitudes of absolute rotatory strengths.

These successful analyses were not achieved uniquely, however. We observe correlations between acceptable values of all e_x , $e_{\pi\sigma}$, and t_x parameters, undoubtedly reflecting the highly parametrized nature of the model. Within that correlated region of parameter space, however, all good reproduction of experiment is charac-

Table I. Optimal Parameter Sets Affording Quantitative Reproduction of "d-d" Transition Energies, Spectral Absorbance, and Rotatory Strengths in CoN₂Cl₂ Chromophores^b

units ^a	param	sparteine	α -sparteine	propylene-diamine	
a	$e_{\sigma}(\text{Cl})$	4000	4100	3800	
	$e_{\pi}(\text{Cl})$	1300	1300	1100	
	$e_{\sigma}(\text{N})$	4800	5000	4250	
	$e_{\pi\pi}(\text{N})$	20	75	75	
	$e_{\pi\sigma}(xz)(\text{N})$	-400	-300	-250	
	$e_{\pi\sigma}(yz)(\text{N})$	180	150	300	
	$e_{\pi\sigma}(yz)(\text{N})$	+100	+200	-300	
	B	750	750	720	
	ζ	450	500	450	
	b	$P_{t_{\sigma}}(\text{Cl})$	85	129	102
		$F_{t_{\sigma}}(\text{Cl})$	22	9	0
$P_{t_{\pi}}(\text{Cl})$		78	82	86	
$F_{t_{\pi}}(\text{Cl})$		9	12	18	
$P_{t_{\sigma}}(\text{N})$		100 ^c	100 ^c	100 ^c	
$F_{t_{\sigma}}(\text{N})$		38	35	33	
$P_{t_{\pi\pi}}(\text{N})$		57	74	64	
$F_{t_{\pi\pi}}(\text{N})$		18	19	19	
$P_{t_{\pi\sigma}}(\text{N})$		58	83	52	
$F_{t_{\pi\sigma}}(\text{N})$		3	12	17	
c		k	0.82	0.85	0.85

^a Units: (a) energies/cm⁻¹; (b) arbitrary units of dipole moment; (c) no units. ^b Local Co-N axis frames (see Figures 4 and 6) defined with z parallel to Co → N and y perpendicular to the plane CoNCl or equivalent: positive xz quadrants contain the triads CoNC. ^c Fixed values.

terized with orbital reduction factors close to 0.9, a value that compares well with experience from a large body of paramagnetic susceptibility analysis. At the same time, the nonuniqueness of the earlier intensity fits is removed: that is, overall good fits now lie within a single and contiguous region of parameter space. The signs of the $e_{\pi\sigma}$ parameters defining good fit are entirely consistent with the proposed location of the bent Co-N bonds. These signs are defined with respect to the quadrant of the local xz (or yz, as appropriate) frame toward which the " σ " bond is displaced, as described elsewhere,³⁸ details of definitions used in the present analyses are included in Table I.

The parametrization of the bent bonding described so far has been totally free, involving e_{π} , $e_{\pi\sigma}$, and $L_{t_{\pi}}$ independently for both xz and yz planes of each Co-N ligation. However, one might expect that the misdirected valency could be represented adequately within a single plane lying between xz and yz. The six parameters $\{e_{\pi}, e_{\pi\sigma}, L_{t_{\pi}}\}_{x,y}$ are then replaced by four $\{e_{\pi}, e_{\pi\sigma}, L_{t_{\pi}}\}_x$ and ϕ , an angle defining the plane, x'z', containing the bent Co-N bond. But these bent bonds may not lie exactly in a plane but rather be somewhat chiral. This would imply an effective angle, ϕ , that varied with distance, r , from the metal. Now the radial integrals implicit within both e and t parameters sum contributions that vary with r in different ways (see, for example, paragraph 5 of ref 6), so that the "mean effective" ϕ values for each parameter would, in general, differ. We have not, therefore, investigated the smaller parameter set further.

Optimal parameter values determined in these analyses are presented in Table I. Detailed comparisons between observed and calculated transition energies, absorption intensities, and rotatory strengths for the sparteine chromophores are made in Tables II and III and illustrated in Figure 5.

B. Dichloro(+)-N,N,N',N'-tetramethyl-1,2-propylenediamine]cobalt(II). Parametrically, this chromophore is entirely similar to the two sparteine systems above. Geometrically, however, the donor atoms very nearly define orthogonal mirror planes,³⁴ and yet the overall CD rotational strengths are of magnitudes similar to those observed for the sparteine molecules characterized by the 19 and 6° rotations of the ClCoCl planes from the normals to NCoN. Despite obvious expectations engendered by the preceding analyses, we developed the present analysis independently and repeated the same simple stages as before. The results were qualitatively identical. No reproduction

Table II. Dichloro(-)- α -isoparteine]cobalt(II): Comparisons between Observed Spectral Data and Those Calculated with the Optimal Parameter Set in Table I

transition energy/cm ⁻¹	rel intens ^a		$I_L - I_R^b$		
	obsd ²	calcd	obsd ²	calcd	
18400	18769	46	45	-14	-11
	18748				
16000	16386	38	38	+7	+8
	16274				
	16009				
	15922				
10000	9814	5	9	+17	+15
	9760				
7600	7537	9	7	+8	+5
	7402				
6400	7086	2	1	-40	-40
	7013				
4100	4052	1	0.3	+67	+63
	3971				
2900	2886	0.7 ^c	0.3	-7	-11
	2783				
	1972				
	1825				
	53				
	0				

^a For solution data: absolute absorbances reported in ref 2. ^b Areas under reported² CD curves for absorption differences between left (L) and right (R) circularly polarized light. Listed ($I_L - I_R$) values equal $1.3 \times 10^{36} R_{gn} \nu_{gn}$, where R_{gn} is the rotatory strength of the transition $g \rightarrow n$, with frequency ν_{gn} in cm⁻¹. ^c Estimated by subtraction of proven² C-H stretching vibration: not included in fitting procedures.

Table III. Dichloro(-)-sparteine]cobalt(II): Comparisons between Observed Spectral Data and Those Calculated with the Optimal Parameter Set in Table I

transition energy/cm ⁻¹	rel intens ^a		$I_L - I_R^b$		
	obsd ¹	calcd	obsd ¹	calcd	
18200	18367	84	84	-10	-10
	18344				
16000	16676	9	9	+5	+3
	16612				
	15891				
	15849				
10600	10460	4	4	+8	+12
	10428				
7700	7746	9	9	+3	+4
	7674				
6500	6539	2	3	-29	-28
	6488				
ca. 4000	4190	1	1	+23	+25
	4058				
	3562				
	3515				
2500	2710	1	1	-1	-1
	2590				
	24				
	0				

^a For solution data: absolute absorbances reported in ref 1. ^b Areas under reported¹ CD curves as differences between absorptions for (L) and right (R) circularly polarized light. Listed ($I_L - I_R$) values equal $10^{36} R_{gn} \nu_{gn}$ where R_{gn} is the rotatory strength of the transition $g \rightarrow n$, with frequency ν_{gn} in cm⁻¹.

of the CD spectrum was possible without both sets of parameters relating to misdirected valency in local xz and yz planes. With both sets, however, a correlated region of polyparameter space afforded excellent quantitative reproduction of all experimental spectral data. The parameters for the xz planes are again related to the small NCoN angle (88°) that results, quite typically, from the five-membered chelate ring and are of physically appropriate signs. Those for the yz planes are of signs corresponding to bent, perhaps chiral, bonds again disposed in the sensible physical arrangement shown in Figure 6. That groups of parameters

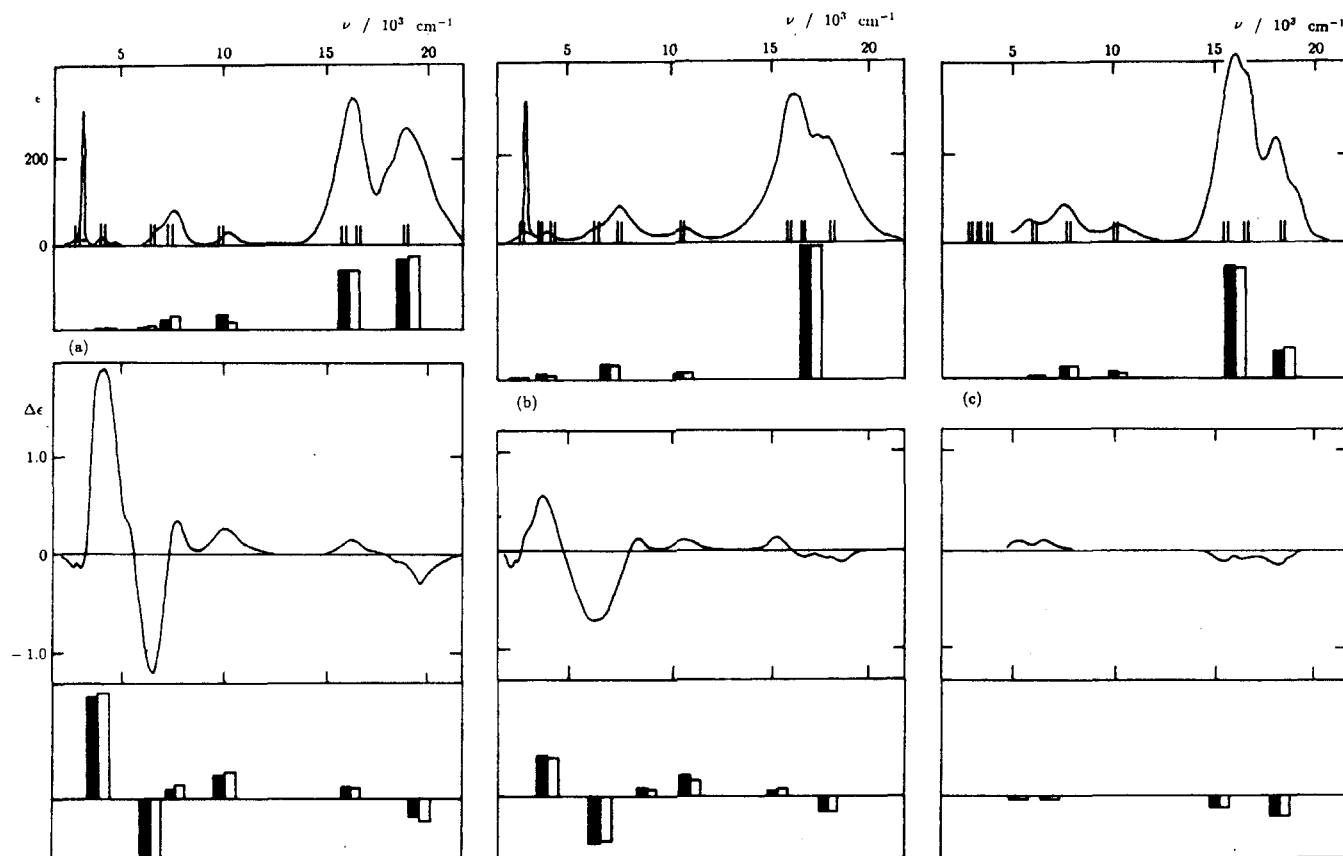


Figure 5. Comparisons between observed transition energies, intensities, and circular dichroism and those calculated with the parameter values of Table I for (a) the α -isoparteine chromophore, (b) the sparteine chromophore, and (c) the propylenediamine complex. Open areas represent observed quantities; filled areas show corresponding calculated ones.

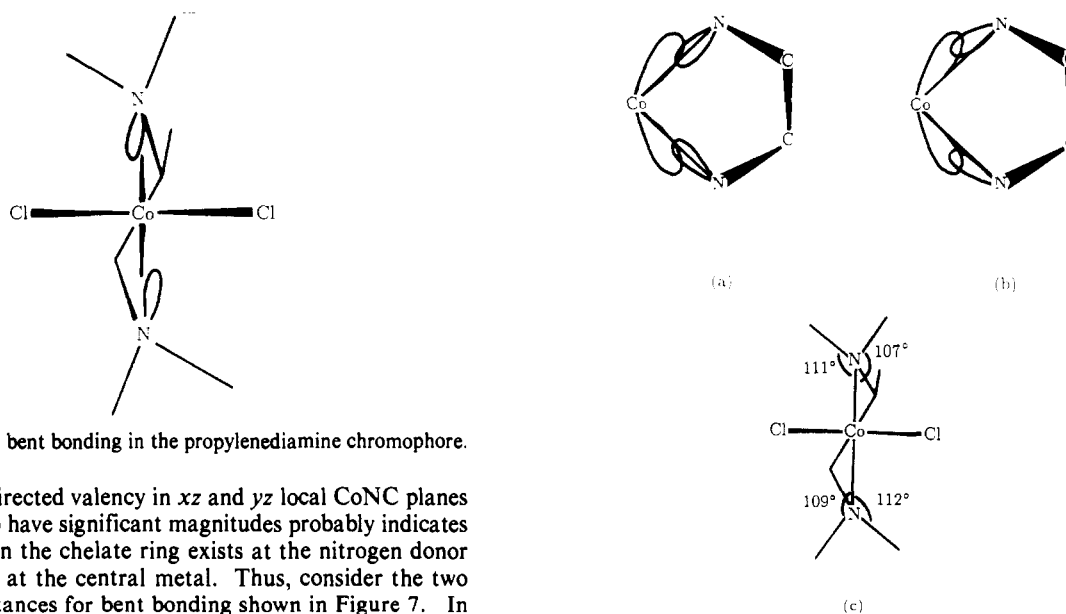


Figure 6. Proposed bent bonding in the propylenediamine chromophore.

referring to misdirected valency in xz and yz local CoNC planes are *both* found to have significant magnitudes probably indicates that ring strain in the chelate ring exists at the nitrogen donor atoms as well as at the central metal. Thus, consider the two possible circumstances for bent bonding shown in Figure 7. In Figure 7a is illustrated the situation that would result from the tetrahedral disposition of the metal orbitals but with nitrogen donor hybrids directed exactly along the line of centers. In this case, the resulting bent bonding lies only in the plane of the paper (xz) and gives rise to $e_{\pi\sigma}(xz)$, $e_{\pi x^2}$, and $L^2_{\pi x}$ parameters only. On the other hand, if, as in Figure 7b, the nitrogen donor orbital is not directed exactly toward the metal atom, as a result of local ring strain, a component of bent bonding normal to the plane of the diagram arises because the carbon atom bonded to the nitrogen does not lie in the plane defined by Co, N, and the cobalt orbital. A further contribution to bent bonding in the yz plane might arise from chelate twisting. While there is some evidence for this from the angles methyl-N-Co, shown in Figure 7c, differences between these angles are probably too small in themselves to explain the

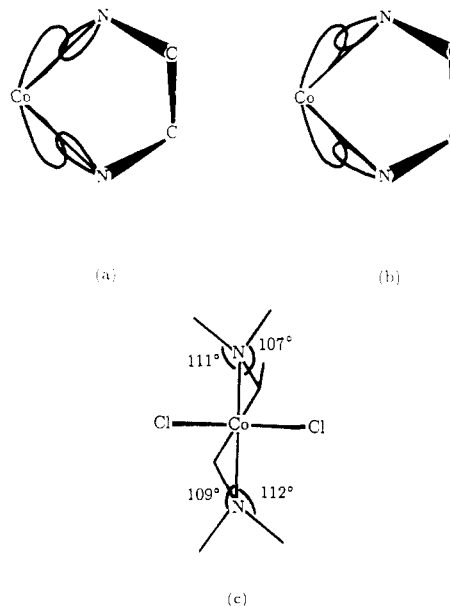


Figure 7. Bent bonding in the propylenediamine complex lying in the plane of the paper (xz) for part a when the donor nitrogen orbital is directed exactly at the metal atom, but having a component normal to this in part b when the donor nitrogen orbital is misdirected. (c) Methyl-nitrogen-cobalt angles.

analytical finding that bent bonding parameters in the yz plane are similar in magnitude to those in the xz plane.

Best-fit parameter values are given in Table I and comparisons with experiment in Table IV and Figure 5.

C. Checks on the t Parametrization of Misdirected Valency. The lowering of a local ligation pseudosymmetry from C_{2v} to C_s symmetry that accompanies misdirected valency is recognized³⁸ in the energy parametrization with $e_{\pi\beta}$ and $e_{\pi\sigma}(\beta z)$; $\beta = x$ or y .

Table IV.
Dichloro[(+)-*N,N,N',N'*-tetramethyl-1,2-propylenediamine]-cobalt(II): Comparisons between Observed Spectral Data and Those Calculated with the Optimal Parameter Set in Table I

	transition energy/cm ⁻¹		rel intens ^a		$I_L - I_R^b$	
	obsd ³	calcd	obsd ³	calcd	obsd ³	calcd
18000	17509	17477	20	18	-12	-12
	16387					
16100 sh	16328	15329	70	71	-7	-7
	15301					
15500	10009	9977	3	4	0	+1
10000	9977					
	7701	7635	6	6	+2	+2
7500	7635					
	6325	6298	2	1	+2	+2
6000	6298					
	4238					
	4030					
	3931					
	3867					
	3510					
	3305					
	12					
	0					

^a From solution data with absolute absorbances reported in ref 3.

^b $(I_L - I_R) = 10^{37} R_{gn} \nu_{gn}$.

Within the intensity parametrization, the principal monitors are the corresponding $L_{t_{\alpha\beta}}$ ($L = P, F$) parameters.¹⁵ All of these have been included in the present analyses, as discussed in the preceding sections. However, the consequences of misdirected valency for the electric-dipole transition moments are actually more extensive, as described recently.¹⁵ We have argued from both theoretical and empirical viewpoints that these further details are likely to contribute only marginally to the intensity modeling in practice, concluding, however, that explicit checks on this view should be made in each new analysis. We have, therefore, performed a number of fresh optimizations for all three of the present chromophores with inclusion of the $\{\alpha\}$ parameters of ref 15. With α values in the range $-0.05 \leq \alpha_i \leq +0.05$, good reproduction of all experimental data is possible for each chromophore. Optimizations identify closely similar regions in t -parameter space, occasionally with a change in some t values by 20. Outside that range for α , best fits become increasingly unsatisfactory. Qualitatively, this behavior is entirely similar to that observed¹⁵ in the earlier study. We therefore report the optimal parameter values of Table I but note that uncertainties of between 10 and 20 are to be assigned to these values arising from the simplified treatment of the misdirected valency. The qualitative conclusions we now summarize are not affected by this degree of uncertainty.

Summary

We have analyzed good quality absorption and CD spectroscopic data for these three *pseudotetrahedral* CoN_2Cl_2 chromophores: the CD data for the two sparteine molecules are particularly noteworthy for their extensive reach into infrared frequencies. Together they provide a worthy test of the cellular ligand-field method to reproduce absorbance and rotatory strengths quantitatively and to provide physically sensible views of the underlying electron density distributions. Earlier analysis^{1,2} of the sparteine data was broadly unsuccessful in reproducing the observed CD traces for the "d-d" transitions. Quantitative reproductions of the CD of a number of lanthanide chromophores have been achieved by Richardson and his colleagues, (e.g. refs 41 and 42). Similar successes have been reported⁴³ for the CD

spectra of various near-octahedral cobalt(III)-amine systems, by Mason in particular.

The present analyses are the first applications of the CLF model, which is a general approach in the sense of being applicable to chromophores with any d^n configuration, any coordination number, or any geometry. We have chosen to begin with these near-tetrahedral systems in which intensity is deemed to arise through the odd part of the static ligand field. We shall report on vibrationally dominated systems in a later article. We believe that the strength and chemical utility of our approach resides in the simple inbuilt relationships that exist between the parametric structure and chemically visualizable elements of electron distribution in chromophores. In the present study, those relationships are manifested (i) in the physicality of the signs of the energy and intensity parameters with respect to detailed coordination geometry and (ii) in the continued acceptability of the relative magnitudes of both e and t parameters as experience with the new model grows.

With respect to point i: the signs of the $e_{\alpha\sigma}$ parameters consistently correlate with the idea of rotated, bent bonding between cobalt and amine ligands. It seems clear that the primary cause for such displacements of bond density from the internuclear axes is the minimizing of electron-electron repulsion for the bonding electrons in the congested regions close to the bonded atoms. Both nitrogen and cobalt are engaged in forming four electron-pair bonds, and we expect these to assume a near-tetrahedral disposition near the atoms. Steric forces originating further out in the coordination shell—deriving from the formation of five-membered chelate rings and the bulk of the rigid sparteine ligands—oblige these tetrahedrally disposed electron densities to compromise in the regions between the bonded atoms and so form the rotated, and possibly chiral, bonds we propose. In the sparteine species, this bond twisting is such as to reduce the chromophore chirality from that suggested simply by the nuclear coordinates of the donor atoms: it also appears responsible for the fact that the observed magnitudes of the CD in these two chromophores are similar, despite the angles between the ClCoCl and NCoN planes being considerably different. In the propylenediamine complex, the bond twisting determined by the ligand chelation and the tetrahedral environment endows the chromophore with a chirality not expected by reference to the donor atom coordinates alone. All this has been inferred within a basic ligand-field approach (with all that entails⁸⁻¹¹) where *explicit* reference is made only to the first coordination shells.

The idea that misdirected valency (bent bonding) might be probed by the measurement of rotatory strengths seems to have begun with Liehr¹⁸ in 1964. It was implemented, however, within the sort of overly approximate molecular orbital scheme favored at that time, and as shown, in one case at least, by Piper and Karipedes,¹⁹ that kind of modeling is quantitatively inadequate. On the other hand, misdirected valency in transition-metal complexes is well evidenced by several recent ligand-field studies:³⁸⁻⁴² these have been reviewed very recently.⁴⁵ Modern ligand-field theory recognizes the dominance of the bonding electron density as the source of the ligand-field potential. It is reassuring to observe the consistency of the present study with this viewpoint in that the magnitudes of the spectral chiralities in the sparteine complexes reflect the location of the cobalt-nitrogen *bonds* rather than of the nitrogen donor *atoms*.

Our approach in this work might be considered in two parts. In the first, we parametrize electric-dipole moments in local environments about the central metal, and in the second, we provide a qualitative interpretation of those optimal parameters. To some extent the two stages are interlinked. This is because of the restrictions imposed on the local parametrization. The various e and t parameters are limited to σ , π_x , π_y , $\sigma\pi_x$, and $\sigma\pi_y$ types for reasons that are part and parcel of the parametric interpretation. If the sources of chirality are indeed located primarily

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in spatial regions close to the metal—one might even say, if the chromophore is “intrinsically” chiral—as argued here in terms of misdirected valency, this interdependence of parametrization and interpretation seems especially apt. On the other hand, in systems—which are not at all exemplified by the present study—where chirality appears to be sourced in rather distant structures—in the “second” coordination shell or even within a chiral solvent (as in DICD studies, for example)—and where a “through-space” rather than a “through-bond” mechanism carries most credence, the present approach is likely to be less appropriate and probably less successful. We must emphasize once more, therefore, that the approach here is part of a ligand-field scheme in which parameters refer directly to orbital admixtures into the d basis—and thence parametrized within effective operators. Formalistically, no doubt, distantly sourced, “through-space” perturbations could be included within such effective operators but only if the sort of local restrictions we adopt are withdrawn

and then, of course, with a consequent loss of local (inner coordination shell) chemical correlation.

The internal consistency of the model with respect to the magnitudes (point ii) of the e and t parameters is also encouraging. For example, the $e_{\sigma}(\text{Cl})$ and $e_{\sigma}(\text{N})$ values for the three chromophores, as listed in Table I, uniformly indicate somewhat better amine σ donation than chlorine. The $e_{\pi}(\text{Cl})$ values also show a consistent pattern that accords well with experience.^{5,9} While the magnitudes of the remaining e and t parameters are somewhat uncertain in view of the correlations discussed earlier, they are consistent throughout the series; not least in that ${}^P t$ contributions appear to be larger than ${}^F t$ for both σ and π interactions and for Co-N and Co-Cl ligations.

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Energies, Intensities, and Circular Dichroism of d-d Transitions in Trigonal-Bipyramidal Cobalt(II) and Nickel(II) Chromophores[†]

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The energies, electric-dipole absorbances, and rotatory strengths of “d-d” transitions in a series of nominally trigonal-bipyramidal chromophores have been reproduced quantitatively within the cellular ligand-field (CLF) approach. The series comprise $M(S\text{-tan})X$ with $M = \text{Co(II)}$ or Ni(II) , $X = \text{NCS}, \text{Cl}, \text{Br},$ or I , and $S\text{-tan}$ is the tripodal triamine $\text{Me}_2\text{NCH}_2\text{CH}(\text{Me})\text{N}(\text{CH}_2\text{CH}_2\text{NMe}_2)_2$. Separate analyses of the three spectral properties have established CLF energy parameters, e_{λ} , and electric-dipole transition moment parameters, ${}^L t_{\lambda}$, that describe a consistent pattern of electron distribution throughout the series. It is argued that the circular dichroism, originating in the $\delta\delta\delta$ conformation of the tripodal ligand, arises through slight bent bonding between the equatorial amines and the central metal. This misdirected valency is monitored with small values of the local e_{σ} CLF parameters or by small values of ${}^L t_{\sigma}$ parameters for the equatorial ligations.

Introduction

In 1985, Utsuno et al.¹ described the synthesis and characterization by X-ray crystallography and electronic spectroscopy of a series of trigonal bipyramidal complexes incorporating a new tripodal tetraamine, $S\text{-tan}$. The ligand $S\text{-tan}$, $\text{Me}_2\text{NCH}_2\text{CH}(\text{Me})\text{N}(\text{CH}_2\text{CH}_2\text{NMe}_2)_2$, which closely resembles the tripod Me_6tren , $\text{N}(\text{CH}_2\text{CH}_2\text{NMe}_2)_3$, adopts a chiral conformation within the complex ions $[M(S\text{-tan})X]^{n+}$ for $M = \text{Co(II)}$ or Ni(II) and $X = \text{NCS}^-, \text{Cl}^-, \text{Br}^-$ or I^- among others. Utsuno et al. reported absorption and circular dichroism (CD) spectra for the “d-d” transitions in all members of these series of complexes and discussed the qualitative features of the CD spectra in terms of selection rules for electric and magnetic dipole moments under C_{3v} symmetry. As part of a program to extend the reach of ligand-field analysis, we report here on the *quantitative* reproduction of both absorption and rotatory strengths in these complexes.

Computation of the absorption intensities requires an evaluation of electric-dipole matrix elements: these, together with magnetic-dipole elements, are needed for a calculation² of the rotatory strengths provided by the CD experiment. Ligand-field theory in general and our recent extensions³⁻⁵ of it in particular offer means of expressing both electric- and magnetic-dipole matrices within the same d -function basis that is conventionally employed in the calculation of transition energies. Inevitably, in view of the very great difficulty in implementing any satisfactory *ab initio* calculation of ligand-field properties throughout the transition series, the approach is parametric. A parametrization scheme

may have utility beyond the mere reproduction of observables, however difficult that often is, only if it is defined directly in terms of physically comprehensible quantities. To date, the best parametrization structures by this criterion are those exploiting a principle of spatial superposition rather than of a global multipole expansion. Contact with chemical bonding and structure is minimal when the $10Dq$ or Δ_{oct} parameters of the global (molecular) decomposition of a ligand field are used and is even less for molecules with little or no symmetry. On the other hand, the separation of σ - and π -bonding factors from each individual ligand in a complex, as first effected within the angular overlap model (AOM)^{6,7} but subsequently and more properly within the cellular ligand-field (CLF) model,^{3,8,9} has brought to ligand-field analysis the familiar notion of the functional group, together with interpretations—and hence exploitations—of all ligand-field properties that are made by using mainstream chemical vocabulary. Furthermore, necessary approximations and assumptions

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