

[Co(3,2,3-tet)Br₂]Br, 53567-37-6; (-)-*trans*-R,R-[Co(3,2,3-tet)-(NO₃)₂]NO₃, 53625-64-2; (+)-*trans*-R,R-[Co(3,2,3-tet)(NCS)₂]ClO₄, 53625-66-4; (-)-*trans*-R,R-[Co(3,2,3-tet)(N₃)₂]ClO₄, 36490-58-1; (-)-*trans*-R,R-[Co(3,2,3-tet)(NH₃)₂]Cl₃, 53625-67-5; (-)-*trans*-R,R-[Co(3,2,3-tet)(NO₂)Cl]ClO₄, 53625-69-7; (-)-*trans*-R,R-[Co(3,2,3-tet)(NO₂)Br]ClO₄, 53625-71-1; (-)-*trans*-R,R-[Co(3,2,3-tet)(NO₂)NCS]ClO₄, 53625-73-3; (+)-*trans*-R,R-[Co(3,2,3-tet)(NO₂)N₃]ClO₄, 53625-75-5; *trans*-R,R,S,S-[Cr(3,2,3-tet)Cl₂]Cl, 53567-41-2; *trans*-R,R-[Cr(3,2,3-tet)Cl₂]BCS, 53625-77-7; (-)-*trans*-R,R-[Cr(3,2,3-tet)Cl₂]ClO₄, 53625-78-8; (+)-*trans*-S,S-[Cr(3,2,3-tet)Cl₂]ClO₄, 53625-80-2; *trans*-R,R,S,S-[Rh(3,2,3-tet)Cl₂]Cl, 53567-42-3; *trans*-R,R-[Rh(3,2,3-tet)Cl₂]BCS, 53625-82-4; (-)-*trans*-R,R-[Rh(3,2,3-tet)Cl₂]NO₃, 53625-83-5; (+)-*trans*-S,S-[Rh(3,2,3-tet)Cl₂]NO₃, 53625-85-7; (3,2,3-tet), 10563-26-5; 1,2-dibromoethane, 106-93-4; 1,3-diaminopropane, 109-76-2; *trans*-[Rh(py)₄Cl₂]Cl, 14077-30-6.

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Conformational Dissymmetry. Circular Dichroism Spectra of a Series of Complexes Containing a Quadridentate Amine Ligand

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The circular dichroism spectra associated with the d-d transitions of an extensive series of conformationally dissymmetric metal complexes are recorded. All of the complexes are of the general type *trans*-R,R-[M(3,2,3-tet)XY]ⁿ⁺, where 3,2,3-tet is a linear quadridentate amine, where M = Co(III), Cr(III), and Rh(III), and where, for the Co(III) complexes, the X and Y axial ligands represent a wide variety of types. It was found that the general form of the circular dichroism patterns exhibited by the d-d bands was extremely sensitive to the environment of the complex and to the nature of X and Y. The type of spectrum observed was dependent on the way the axial groups split the upper state d-electron manifolds, but for any given complex, large variations in the circular dichroism were observed from one solvent to another and in the solid state. These environmental variations are ascribed to varying amounts of donor atom distortions and possibly also to changes in the twist sense of the donor atom displacements. Dissymmetric solvation and, in appropriate cases, dissymmetric rotamer orientations of the axial groups are also considered as contributing factors. In view of these variations, the problems associated with deriving regional rules for conformational isomers are discussed.

Of all the stereochemical properties of molecules the assignment of absolute configuration remains the single most intractable feature which is not subject to routine physical methods for its elucidation. While it is true that, for certain restricted and closely specified systems, correlations between chirality and circular dichroism show a consistency necessary for the advancement of predictive regional rules, it is also true that these quasiempirical rules encompass only a limited number of chromophores and structural types.¹ Even the purely theoretical methods,²⁻⁵ which are unambiguous in principle, require a very detailed knowledge of both the electronic and nonchiral structure of the molecule.

Unlike the studies of organic chromophores where detailed and extensive studies have been made, no comparable systematic effort has been reported for the correlations between absolute configuration and the circular dichroism of the d-d transitions of transition metal complexes. Despite this, regional rules, purporting to correlate structure with absolute configuration, have been put forward for these systems with disconcerting profusion. Not surprisingly, few of these have proved to be general or revealing.

The problems associated with deriving regional rules for the d-d bands of transition metal chromophores are generally more

complicated than those encountered for many of the organic chromophores. The most obvious complication is the fact that d-d transitions show a high orbital multiplicity in their upper states and these components almost invariably show a variety of sign patterns within the closely spaced upper state manifolds. The circular dichroism, thus observed, is a result of overlapped bands of varying signs and intensities, a proper interpretation of which would require a knowledge of the separations between assigned levels, the individual band shapes, the individual signs, and the individual intensities. Partly because of this problem, a prevalent device has been simply to use the sign of the "major band" associated with a particular manifold of transitions as the correlative index for assigning configurations. It is not difficult to see, however, that the sign of the major band would reverse simply because of variations in the circular dichroism intensities of overlapped transitions even if, for a series of complexes of the same absolute configuration, the spacings between levels and the signs of the components were the same. It is not surprising, therefore, that the major band hypothesis has proved to be of little value for configurationally dissymmetric complexes and we show here that the same applies for conformationally dissymmetric compounds.

The present series of papers is an attempt at providing

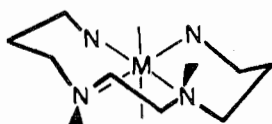


Figure 1. The absolute configuration of the *trans-R,R*-[Co(3,2,3-tet)XY]⁺ ion. All the circular dichroism spectra in this paper refer to this absolute configuration.

circular dichroism data for a comprehensive series of dissymmetric complexes which owe their asymmetry solely to conformational chirality. Two basic themes have been pursued: the first relates to the effects observed in the circular dichroism spectra of a homologous series of complexes, when, what might be supposed, trivial substitutions are made at the central metal atom; the second concerns whether solvent-induced variations in circular dichroism are a reflection of conformational changes or simply changes in the intensities and, perhaps, even signs of the closely overlapped manifolds.

Before we begin, we briefly allude to two recent papers^{6,7} concerning the d-d circular dichroism of conformationally dissymmetric complexes which provide a basis for the subsequent discussion. The first of these⁶ addressed itself to a number of problems—the nature, symmetry, and sign of the dissymmetric potential, the various structural elements of asymmetry which are partly contingent but which can be separated and identified, the problem of obtaining “hypothetical gas” circular dichroism spectra, and the origins of the differing signs observed for various components of the T_{1g} manifold. The pseudoscalar potential proposed was probably physically unrealistic, except for exchange interactions, because of the extremely sharp distance dependence (r^{-19}) of the potential. Whatever the merits or otherwise of this potential, it did provide a convenient focus from which the other problems could be discussed. The basic arguments presented in the paper, however, could equally well have been applied to derive more physically realistic pseudoscalar potentials; these were the subject of the second paper.⁷ Although this second paper offered more reasonable potentials and covered both configurational and conformational dissymmetry, the crucial problem of a spectroscopic component analysis was avoided by proposing a “net sign” for all the d-d components as a correlative index of absolute configuration. This assumption which is similar to, but somewhat more acceptable than, the “major band” hypothesis was unfortunate because, first, exceptions that invalidate the rule were known at the time and, second, the theoretical framework given, together with the arguments in the first paper, could have been extended to include a component by component assignment. In other respects the paper is important although as we show here the “net sign” assumption fails.

This paper reports the circular dichroism spectra of a series of *trans* complexes derived from the 3,2,3-tet ligand [N-H₂(CH₂)₃NH(CH₂)₂NH(CH₂)₃NH₂]. The subsequent papers will deal with the substituted ligands. All the complexes have the absolute configuration *trans-R,R*-[Co(3,2,3-tet)XY]ⁿ⁺ (Figure 1) and are known with certainty from two X-ray determinations^{8,9} and the chemical correlations given in the preceding paper.¹⁰ The spectra of the homologous Rh(III) and Cr(III) *trans*-dichloro complexes are also recorded.

1. Spectroscopic Considerations

Octahedral spin-paired d⁶ and d³ complexes show two spin-allowed one-electron transitions within the d-electron manifold. Both transitions are triply degenerate; the higher energy promotion, ¹A_{1g} → ¹T_{2g}(d⁶) or ⁴A_{2g} → ⁴T_{1g}(d³), is electric quadrupole allowed while the lower energy one, ¹A_{1g} → ¹T_{1g}(d⁶) or ⁴A_{2g} → ⁴T_{2g}(d³), is magnetic dipole allowed. In octahedral complexes belonging to lower point groups, the zero-order selection rules are largely retained within the

components of each manifold although, formally, distribution of the transition moments between the two manifold transitions is allowed. For “hard” ligands, Moffitt’s¹¹ original postulate that the lower energy transition, because of its zero-order magnetic dipole character, should show stronger circular dichroism than the higher energy transition seems to have been largely sustained by experiment. For this reason and because of the fact that, in many cases, the higher energy band is obscured by charge-transfer bands, the lower energy band has been the subject of most investigations. We will show, however, that Moffitt’s assumption does not hold for many of the complexes described here.

The present series of complexes all have the general chromophore *trans*-[M(N)₄XY]ⁿ⁺, where the donor atom symmetry causes the upper states of the first transition to split into singly degenerate and doubly degenerate components. The singly degenerate transition will occur at the frequency of the parent transition of the [M(N)₆]ⁿ⁺ chromophore and will remain essentially unshifted when X and/or Y are permuted. The position of the doubly degenerate component, however, will shift according to the ligand field strengths of the X and Y ligands in the axial positions. If the axial field is less than the (N)₄ planar field, the doubly degenerate component will appear at lower energies, but if the axial field is stronger than the (N)₄ field, this component will appear at higher energies relative to the singly degenerate transition. These results can be derived and semiempirically quantified by either crystal field¹² or molecular orbital¹³ theories and are fairly accurately confirmed by experiment, at least for “hard” ligands.

In addition to these first-order splittings, an analysis of the circular dichroism spectra requires a recognition that the degeneracy of the doubly degenerate component can be removed by a variety of more subtle effects in dissymmetric *trans*-[M(N)₄XY]ⁿ⁺ chromophores. These splittings tend to be small, of the order of 100 cm⁻¹ for the ¹A_{1g} → ¹E_g transition of *trans*-[Co(R-pn)₂Cl₂]ClO₄,¹⁴ and are not resolved in the isotropic absorption which is characteristically broad, of the order of 2000 cm⁻¹ at half-bandwidth. If, however, the circular dichroism components carry opposite signs, the splitting may be revealed. The sense and magnitude of this small higher order splitting is not easily determined.

2. *trans-R,R*-[M(3,2,3-tet)Cl₂]⁺ Complexes

In Figure 2 we show the absorption and circular dichroism spectra of the complexes *trans*-[M(3,2,3-tet)Cl₂]⁺, M = Co(III), Cr(III), and Rh(III). The absolute configurations of the cobalt and chromium complexes are known;¹⁰ the configuration of the rhodium complex is based on the fact¹⁰ that all three complexes form the less soluble diastereoisomer with the α -bromocamphor- π -sulfonate (BCS⁻) ion. The assignment is probably correct but not proven by this observation alone. For the cobalt complex, the absorption band at 16,000 cm⁻¹ is the ¹A_{1g} → ¹E_g transition and the band centered at 21,000 cm⁻¹ is the ¹A_{1g} → ¹A_{2g} excitation, both of which are derived from the magnetic dipole allowed ¹A_{1g} → ¹T_{1g}(O_h) transition. The bands around 25,000 cm⁻¹, which are partly overlapped by charge-transfer transitions, are the components of the ¹A_{1g} → ¹T_{2g}(O_h) transition. Both the absorption and circular dichroism spectra of the cobalt complex are recorded in three solvents and the circular dichroism of various salts in KBr disks is also shown. It will be seen that the circular dichroism is strongly dependent on the environment.

In all three solvents the ¹A_{1g} → ¹E_g transition shows essentially negative circular dichroism, whereas the ¹A_{1g} → ¹A_{2g} band is negative in methanol and weakly negative in DMSO, and a plus-minus couplet is observed in this region in DMF.¹⁵ Under the ¹A_{1g} → ¹T_{2g} transition smaller solvent variations seem to occur, but the circular dichroism is of the same order

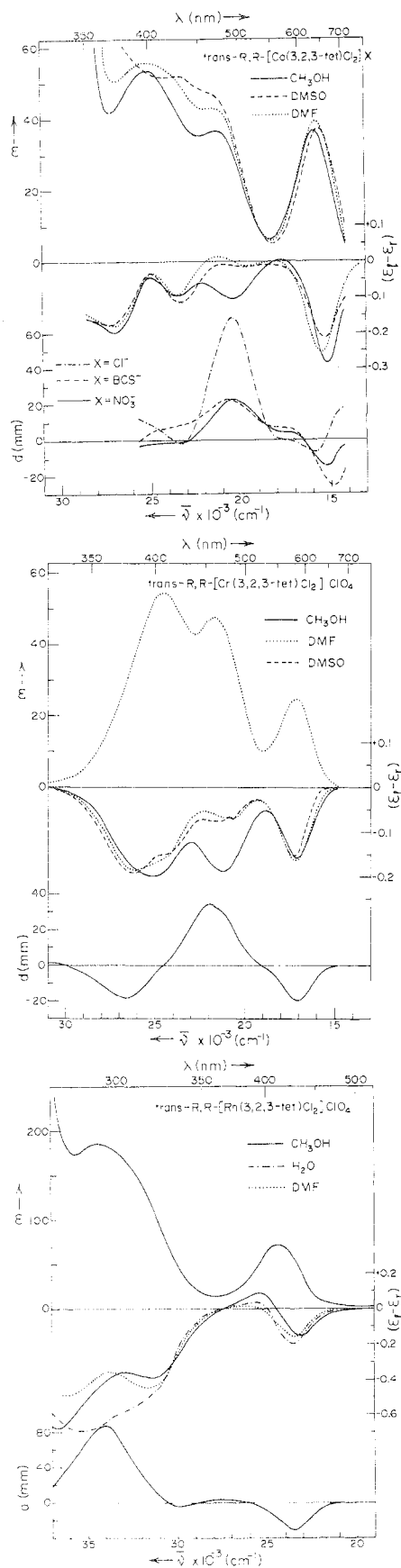


Figure 2. The circular dichroism spectra of the dichloro complexes of cobalt(III), chromium(III), and rhodium(III).

of magnitude as that carried by the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ components. Thus, in this complex Moffitt's (magnetic dipole) selection

rule¹¹ breaks down either because of mixing within the total d-electron manifold or, more probably, because of mixing of the ${}^1T_{2g}$ upper states with those of close-lying charge-transfer states.

We will show in subsequent papers that these solvent-induced variations in circular dichroism are not due to conformational changes, at least not those involving the terminal six-membered rings undergoing chair-skew changes. If this is true, then we are forced to conclude that the effects are due to solvation which may change the energy positions of the bands slightly, cause variations in the relative intensities of the bands, and even, because the solvation on the average must be dissymmetric, change the intrinsic sign of particular bands.¹⁶ On this basis, we interpret the spectra as follows.

We assume that the ${}^1A_{1g} \rightarrow {}^1E_g$ band is split slightly and that the lower energy component carries negative circular dichroism while the higher energy component carries positive circular dichroism but that it is much weaker than the former. If the sense of the splitting remains the same in all three solvents, then in DMF and DMSO the negative component dominates at the exclusion of the other whereas, in methanol, the positive component just becomes detectable. These resultant spectra may be due to small variations in relative intensities of the two individual bands and/or slight differences in splitting with the sense retained. A close inspection reveals that the negative band peaks, in all three cases, are slightly displaced to lower energies compared to the absorption maxima which lends support to our assumptions. It is probable that the ${}^1A_{2g}$ band in all three solvents is negative but, in going from methanol through DMSO to DMF, becomes progressively more overlapped by a positive component of the ${}^1T_{2g}$ manifold. The lowest energy ${}^1T_{2g}$ component in this system is the ${}^1A_{1g} \rightarrow {}^1B_{2g}$ transition which we assign to the negative circular dichroism band at $23,500\text{ cm}^{-1}$; the other component, ${}^1A_{1g} \rightarrow {}^1E_g$, is assigned to the negative band at $27,000\text{ cm}^{-1}$. The origin of the minus-plus couplet in the region $19,000\text{--}22,000\text{ cm}^{-1}$ observed in DMF solution is not clear. It could be due to the presence of a singlet-triplet transition or it could be an artifact due to the wings of overlapping bands although this is difficult to sustain without additional hypotheses about the presence of canceled positive bands which are not observed.

These solvent variations, which are even more pronounced in other homologous complexes, raise the question as to the validity of trying to develop regional rules for these types of complexes. It is clear that, ideally, an environmentally free spectrum would be desirable. In the absence of this, we have measured all the spectra in the solid phase as KBr disks in the hope that this might provide consistent data. As may perhaps have been anticipated, this has not proved to be the case although matters are improved in some respects. We include the solid spectra because structural determinations can provide precise knowledge of the structures and environments of the ions.

The solid-state spectra of the cobalt complex with the counterions Cl^- , NO_3^- , and BCS^- show that in all cases the ${}^1A_{2g}$ band becomes strongly positive whereas it was negative in the three solutions. For the NO_3^- and BCS^- counterions, the 1E_g band shows a low-energy minus component and a higher energy plus component but the Cl^- salt has a plus-minus couplet in the reverse sense. The appearance of couplets tends to support our assumption that the 1E_g circular dichroism in the solutions is the resultant of plus-minus couplets. We suggest that the reversal of the couplet in the solid Cl^- salt is due to the fact that the sense of the splitting of the two 1E_g components has been reversed presumably because of the exigencies of crystal packing.

The absorption and circular dichroism of the chromium

complex are similar to those of the cobalt system except the charge-transfer bands do not intrude and all the one-electron transitions within the d-electron manifold are clearly seen. The linear absorption band at $17,000\text{ cm}^{-1}$ is the ${}^4B_{1g} \rightarrow {}^4E_g$ transition, the one at $21,500\text{ cm}^{-1}$ is the ${}^4B_{1g} \rightarrow {}^4B_{2g}$ excitation, and the band centered around $25,500\text{ cm}^{-1}$ represents the components of the ${}^4A_{2g} \rightarrow {}^4T_{1g}$ transition. Perhaps the most striking feature is that the ${}^4T_{2g}$ and ${}^4T_{1g}$ manifolds carry essentially the same rotational strengths. Because the charge-transfer bands are well separated from the d-d bands, this suggests that, contrary to Moffitt's selection rule, the magnetic dipole character of the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ band is strongly mixed with that of the ${}^4A_{2g} \rightarrow {}^4T_{1g}$ transition.¹⁷ As in the cobalt complex of the same absolute configuration, the ${}^4B_{1g} \rightarrow {}^4E_g$ and ${}^4B_{1g} \rightarrow {}^4B_{2g}$ bands are observed to be negative, and although similar solvent variations occur, no changes in sign occur. The small "kinks" seen in the DMSO and DMF circular dichroism spectra at $20,700\text{ cm}^{-1}$ are probably spin-forbidden transitions derived from the ${}^4A_{2g} \rightarrow {}^2T_{2g}$ transition.^{18,19} The circular dichroism band at $24,500\text{ cm}^{-1}$, seen as a shoulder in DMF, and the band at $26,500\text{ cm}^{-1}$ (in DMF) are probably the ${}^4B_{1g} \rightarrow {}^4A_{2g}$ and ${}^4B_{1g} \rightarrow {}^4E_g$ transitions, respectively, which derive from the ${}^4A_{2g} \rightarrow {}^4T_{1g}$ transition. In the solid, the ${}^4B_{1g} \rightarrow {}^4B_{2g}$ band reverses in sign and is unsymmetrical possibly because of overlap with the spin-forbidden band. There is no evidence that the lower energy 4E_g band carries a two-signed couplet although the data are not inconsistent with the presence of a weak positive higher energy component.

The rhodium complex, however, shows a clear plus-minus couplet for the 1E_g band at $24,000\text{ cm}^{-1}$ in water and methanol and a poorly resolved one in DMF; the solid ClO_4^- salt gives only a negative band. We are unsure of the electronic provenance of the two weak bands at $30,000$ and $28,000\text{ cm}^{-1}$ in the solid spectrum; they might be components of the ${}^1A_{1g} \rightarrow {}^3T_{2g}$ excitation. The ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition of the $[\text{Rh}(\text{NH}_3)_6]^{3+}$ ion occurs²⁰ at $33,000\text{ cm}^{-1}$ and hence the ${}^1A_{1g} \rightarrow {}^1A_{2g}$ transition should occur in this region; it is clear, however, that this band is heavily overlapped both in the solutions and in the solid by bands probably derived from the ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transition. In the solid, this whole manifold of transitions becomes positive unlike the case of the chromium analog. The ${}^1A_{2g}$ component probably lies to somewhat lower energies than the positive band maximum in the solid-state spectrum.

3. Complexes with Weak Axial Fields

Figure 3 shows the spectra of the *trans*-dibromo, -dinitrato, and -diazido complexes where the axial ligand field is much weaker than the in-plane field. Unlike the corresponding dichloro species, the dibromo species shows a clearly resolved couplet under the 1E_g band with the same characteristics as that observed for the rhodium complex. The ${}^1A_{2g}$ band is heavily overlapped by the ${}^1A_{1g} \rightarrow {}^1T_{2g}$ and charge-transfer transitions but is probably represented by the negative shoulder at $21,000\text{ cm}^{-1}$. In the solid, both the ClO_4^- salt (shown) and the Br^- salt retain the minus-plus couplet (in the same sense) but the ${}^1A_{2g}$ band becomes positive.

The dinitrato complex is only stable in methanol; in other polar solvents extensive solvolysis occurs. The 1E_g band shows a strong couplet but in the opposite sense to that observed for the dihalogeno complexes. We suspect that the reason for this is not an inversion of sign of the components but rather that the sense of the splitting is reversed for the nitrate species. The ${}^1A_{2g}$ band at around $21,000\text{ cm}^{-1}$ appears to be weakly negative in solution and unlike the dihalogeno complexes it remains so in the solid. The circular dichroism associated with the ${}^1A_{1g} \rightarrow {}^1T_{2g}$ excitation ($23,000\text{--}28,000\text{ cm}^{-1}$) is weak compared to the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ components which is in conformity with

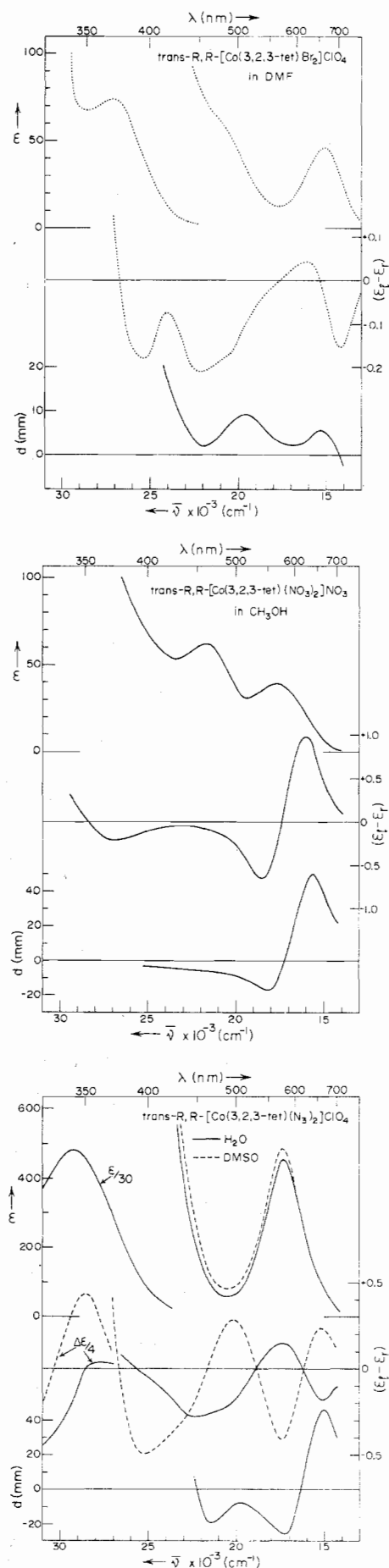


Figure 3.

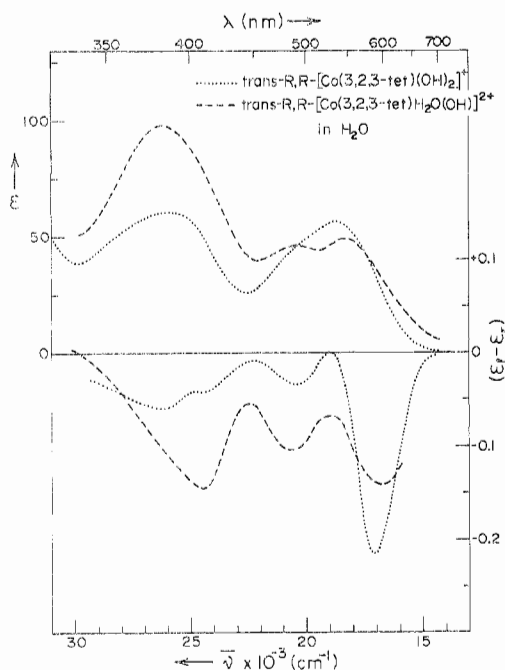


Figure 4.

Moffitt's rule. It is not clear, however, why the rule should hold for this complex but not for the cobalt- and chromium-chloro complexes. Arguments based on mixing-in of charge-transfer bands cannot be convincingly sustained since, for the chromium complex, the charge-transfer and d-d bands are well separated. Similarly arguments which invoke a somewhat greater reduction of interelectronic repulsion for the chloro complexes as opposed to the "hard" oxygen donor systems do not seem to be acceptable because, as we shall see, Moffitt's rule does not hold for the *trans*-hydroxoquo complex.

The diazido complex shows the most spectacular solvent variations of the circular dichroism. In water solution a minus-plus couplet is observed for the 1E_g band at $21,000\text{ cm}^{-1}$ and an overlapped negative ${}^1A_{2g}$ band is observed. An almost enantiomorphic spectrum is observed in DMSO. Water and methanol give similar spectra and DMF gives a spectrum similar to that for DMSO. It would appear that the ${}^1A_{2g}$ band changes sign in the two solvents but this may not be so for the components of the 1E_g band where a reversal of the sign pattern could occur simply by the sense of the splitting changing in the two solvents without a change in sign of the components. We have investigated this sign variation as a function of solvent composition. A solution of 50% water-DMSO by volume gives a circular dichroism spectrum which is almost zero for the band at $17,500\text{ cm}^{-1}$, is slightly negative for the $15,000\text{-cm}^{-1}$ band, and gives a slightly negative ${}^1A_{2g}$ band.²¹ In 75% water-DMSO the spectrum is a weaker imitation of the water spectrum, whereas in 75% DMSO-water, the spectrum is a weaker variety of the DMSO spectrum. We are unsure why there should be a roughly smooth variation in these solvent mixtures because we would not expect the immediate solvation of the complex to be a smoothly varying function of the solvent composition.²² In the solid state a plus-minus couplet is observed for the 1E_g band but, like the dinitrato species and unlike the halogeno complexes, the ${}^1A_{2g}$ is negative.

Figure 4 shows the spectra of the *trans*-hydroxoquo complex in water and the *trans*-dihydroxo complex prepared from the former by dissolution in 0.1 M NaOH . The *trans*-hydroxoquo species racemizes rapidly¹⁰ in neutral water and the circular dichroism was obtained in sections and then extrapolated to zero time. Assuming a reasonable^{23,24} set of acid dissociation constants for the coordinated aquo groups,

a $2 \times 10^{-2}\text{ M}$ solution made up of the solid hydroxoquo complex in neutral water will exist essentially as the hydroxoquo species. It will be seen that both complexes clearly display both the ${}^1T_{1g}$ and ${}^1T_{2g}$ manifolds and that the circular dichroism, particularly for the hydroxoquo species, is of the same order of magnitude under the two transition manifolds. For both complexes the ${}^1A_{2g}$ bands at $21,000\text{ cm}^{-1}$ are negative as is the lower energy 1E_g transition. Because in both cases the circular dichroism is displaced to lower energies compared to the linear absorption for 1E_g , it may be that a weaker positive component lies to higher energies. This tends to be supported by the appearance of "saddles" at $19,000\text{ cm}^{-1}$ which might not be expected when the two negative bands on either side are so closely spaced.

4. Complexes with Medium Axial Fields

Figure 5 shows the spectra of the *trans*-diisothiocyanato, *trans*-nitroazido, *trans*-nitrochloro, and *trans*-nitrobromo complexes. In all these, the axial fields are only slightly weaker than the in-plane field so that the ${}^1A_{2g}$ and 1E_g bands are heavily overlapped although in all cases the 1E_g will lie lower in energy. It is a common observation for Co(III) complexes of the type *trans*-[Co(N)₄XY]ⁿ⁺ that the linear absorption of the 1E_g component tends to be stronger than the ${}^1A_{2g}$ component.²⁵ Whatever the reasons for this, the phenomenological fact is that, generally for systems where the ${}^1A_{2g}$ and 1E_g bands are closely spaced, the band maximum of the ${}^1T_{1g}$ manifold is the same as the absorption maximum of the 1E_g band. For the case of the diisothiocyanato complex, the ${}^1A_{2g}$ band appears as a very weak shoulder at $21,000\text{ cm}^{-1}$ in the linear absorption which is dominated by the 1E_g band at $18,000\text{ cm}^{-1}$.

The circular dichroism of this ion shows complex patterns where in DMSO the 1E_g carries a plus-minus couplet and a positive ${}^1A_{2g}$ band, in DMF the ${}^1A_{2g}$ absorption remains positive but the 1E_g band is negative, and in water 1E_g becomes more negative and ${}^1A_{2g}$ inverts in sign. The solvent variations of the 1E_g band may be due to the negative 1E_g component's becoming progressively stronger from DMSO through DMF to water compared to the positive component. In the solid, however, the 1E_g band carries positive circular dichroism; the ${}^1A_{2g}$ band is negative.

The sense of the splitting pattern for the 1E_g band of the nitroazido complex appears to be reversed compared to that of the diisothiocyanato complex. The minus-plus couplet and a negative ${}^1A_{2g}$ band are observed in both water and DMSO. In the solid, the ${}^1A_{2g}$ band is positive and the 1E_g band gives a single negative component. Thus, if the circular dichroism spectra of the diisothiocyanato and diazido complexes were measured in DMSO and in the solid, it might be supposed that they were of opposite absolute configuration.

The *trans*-nitrobromo and *trans*-nitrochloro complexes rapidly solvolyze in solvents other than DMF. For both complexes, the ${}^1A_{2g}$ bands appear weakly positive but are heavily overlapped. In going to the solid, both the ${}^1A_{2g}$ and 1E_g bands become positive whereas in solution the 1E_g bands were negative.

5. Complexes with Equivalent Axial and Equatorial Fields

When the in-plane and axial ligand fields are almost identical, the relative positions of the ${}^1A_{2g}$ and 1E_g components are almost impossible to calculate. Figure 6 shows the spectra of two such complexes with effectively O_h crystal fields. Under the ${}^1T_{1g}$ band, the *trans*-nitroisothiocyanato complex, unlike the *trans*-diammine species, shows a minus-plus pattern in DMF and in the solid but, like the diammine complex, a plain negative band is observed in water. If we recall that the ${}^1A_{2g}$ band in all the other complexes occurs at $21,500\text{ cm}^{-1}$, then, since the negative bands of the diammine complex and, in DMF and the solid, of the nitroisothiocyanato complex occur

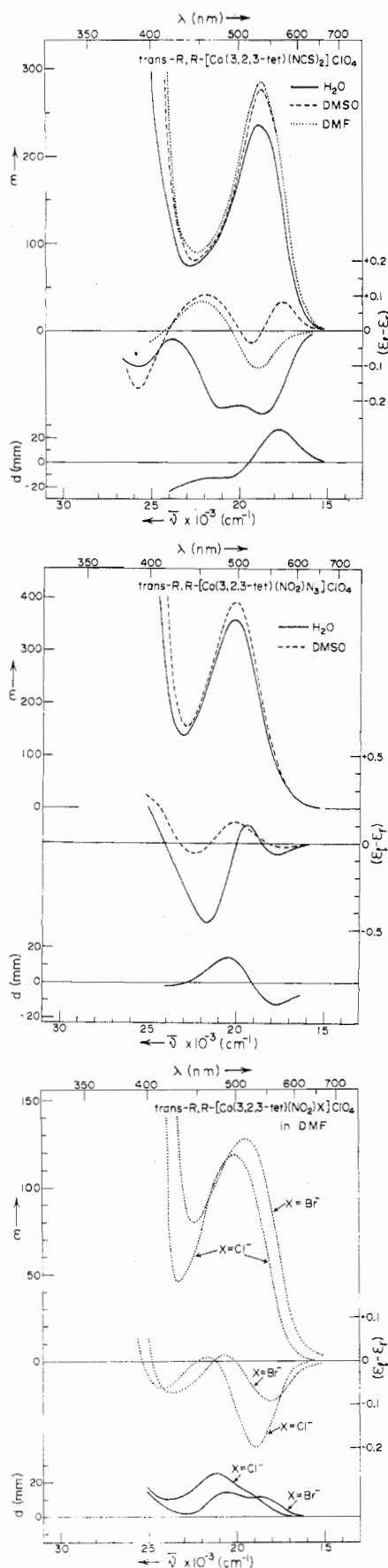


Figure 5.

at lower energies, these are assigned to the 1E_g component. The positive bands of the nitroisothiocyanato complex are

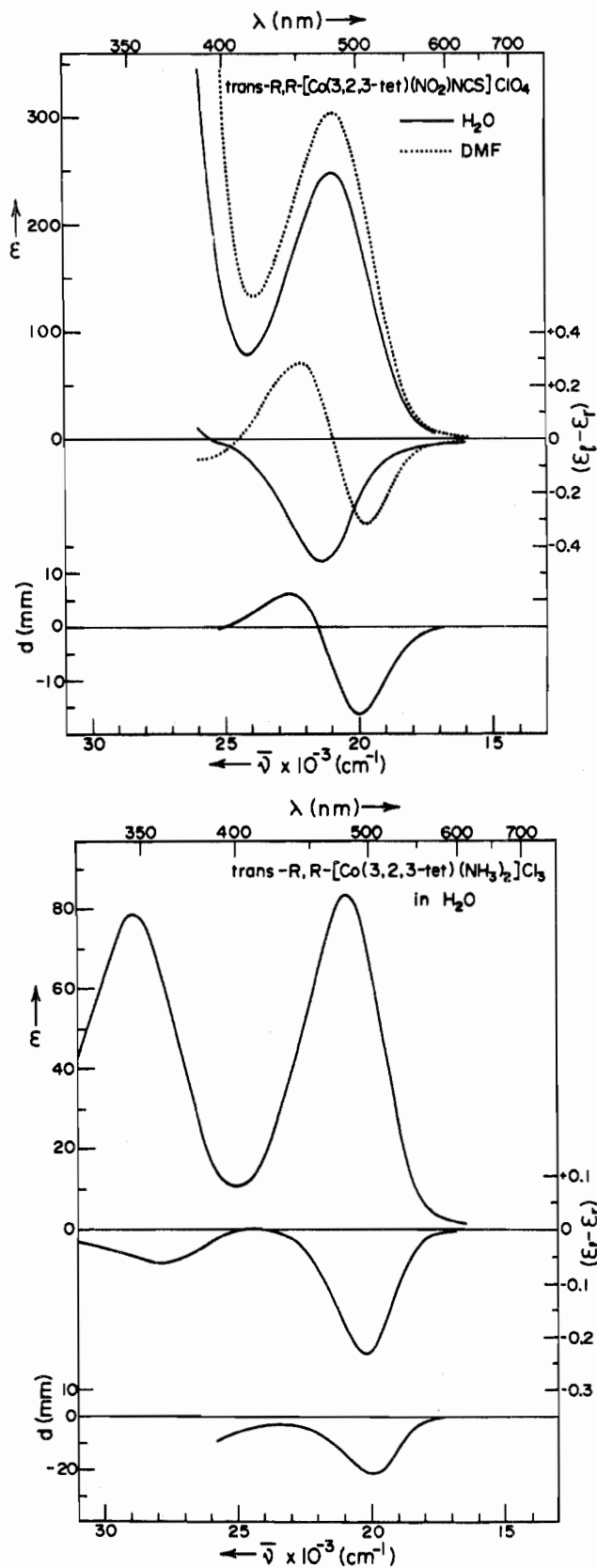


Figure 6.

assigned to the ${}^1A_{2g}$ band. We think that in water the ${}^1A_{2g}$ band for this complex inverts in sign and dominates the spectrum.

6. Complexes with Strong Axial Fields

The dinitro and dicyano complexes both have axial fields which are stronger than the in-plane field, and while the ${}^1A_{2g}$

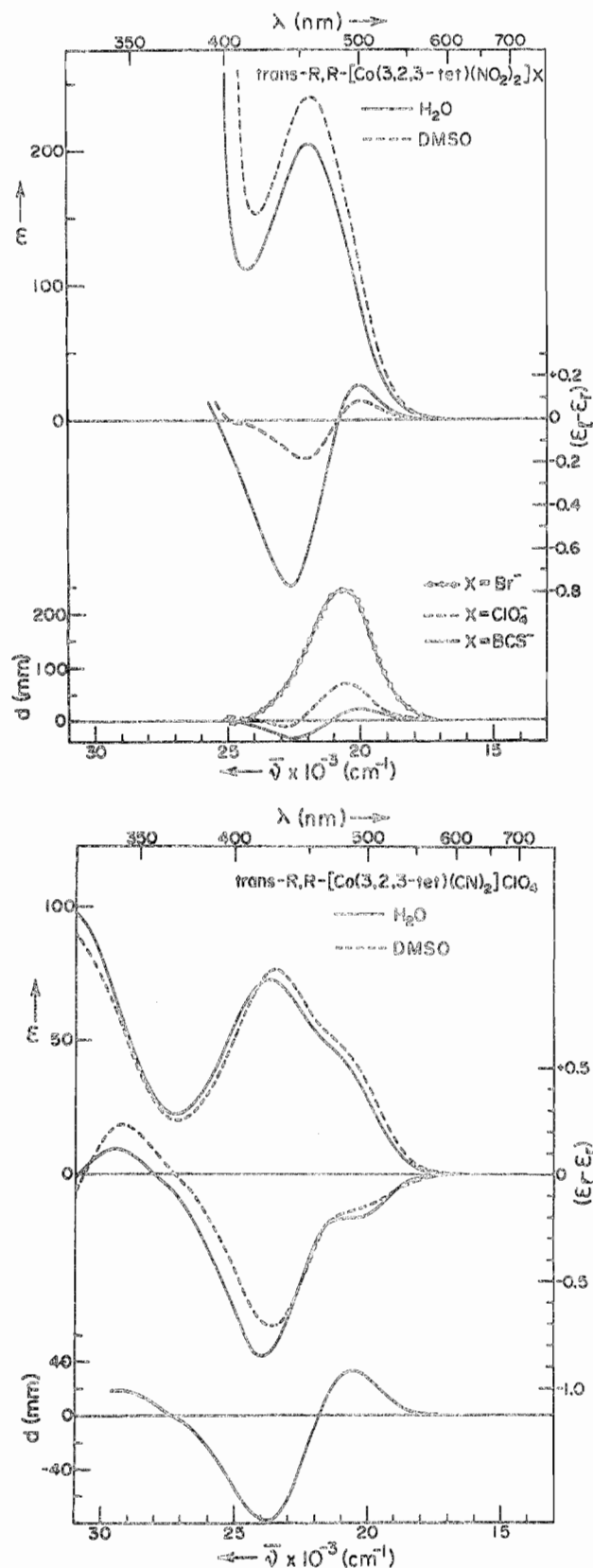


Figure 7.

band will not be shifted, the 1E_g band will appear above it in energy. Figure 7 shows these two spectra where both the dinitro and dicyano complexes show negative circular dichroism for the 1E_g bands, but their respective ${}^1A_{2g}$ bands, at 21,000 cm^{-1} , are of opposite sign. The ${}^1A_{2g}$ band of the dicyano complex reverses sign in the solid, whereas this band of the

dinitro complexes in the solid becomes progressively stronger as the anion is changed from BCS^- through ClO_4^- to Br^- , where in the last it completely dominates the circular dichroism under the ${}^1T_{1g}$ band. We have also investigated the circular dichroism of the solid Cl^- and I^- salts and found these to be similar to the Br^- spectrum.

7. Discussion

The present work represents the first systematic and comprehensive study of conformationally induced circular dichroism of metal complexes and a hitherto unsuspected complexity has been revealed. Even the tacit assumption that the circular dichroism patterns carried by the d-electron manifolds are essentially the result of chiral perturbations of the inner-sphere ligand environment is open to question because of the solvent variations and the crystal packing effects observed. So dramatic are these effects that we were inclined to attribute them to conformational changes involving chair-skew interconversions of the terminal six-membered rings; but as we shall show, similar variations are observed when the terminal rings are fixed in chair conformations by appropriate substituents. This result, which implies that large solvent variations can occur without conformation changes, calls into question some recent suggestions^{26,27} about circular dichroism changes indicating conformational proportions. It also raises the question as to whether there is any reasonable expectation that correlations between circular dichroism and absolute configurations for conformational isomers will be found except for a series of narrowly specified systems. In order to answer this question, the factors which may cause these effects need to be considered.

Many of the variations observed can be explained by invoking changes in the intensities of closely overlapped bands of differing signs and/or by a change in the sense of the splitting of the 1E_g band. As the separation between the ${}^1A_{2g}$ and 1E_g levels is "stretched" out, the variations with the environment tend to be less dramatic than when the ${}^1A_{2g}$ and 1E_g levels are "bunched" together although this is not always so. The probability that the 1E_g band carries, in most if not all cases, a plus-minus couplet which may or may not manifest itself according to relative intensities and separation between the components and which may switch sign according to the sense of the splitting makes the use of this band as a correlative index of absolute configuration a hazardous proposition. Even the ${}^1A_{2g}$ band which is devoid of the complexities of a two-component quasidegenerate transition switches sign from complex to complex and from one environment to another. If correlations do not exist between signs of individual bands and chirality, then one might be tempted to use the overall algebraically summed sign ("net sign") of the whole d-electron manifold or restrict the sum to a particular set of components. It is clear, however, that for these complexes no correlation exists between the "net sign" and configuration for any set of d-d transitions even if it could be decided which environmentally perturbed set of spectra to take; in fact these spectra provide examples of positive, negative, and essentially zero "net signs." Similarly the idea of a "major band" is without consistent meaning.

The environmental variations in circular dichroism suggest that the d electrons are subjected to a number of sources of molecular dissymmetry which, individually, generate opposing circular dichroism in a particular transition. Because the effects are so pronounced, it is probable that contributing factors are in delicate balance. In a previous paper⁶ we suggested that an isolated conformationally dissymmetric complex had two principal sources of dissymmetric perturbation which were of comparable magnitude and which could be opposing in sign for the generated circular dichroism. The first was the obvious puckering of the chelate rings; the second,

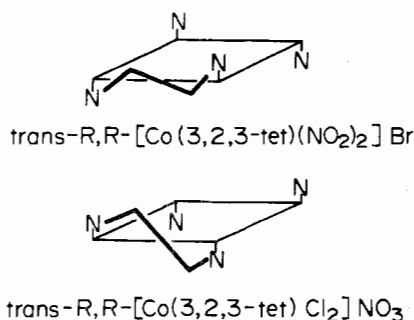


Figure 8. The twist sense displacements of the donor nitrogen atoms with respect to the *trans*-[Co(N)₄] mean plane (see ref 9).

less obvious but probably in many cases as important, was the chiral displacements of the donor atoms. In most cases the conformations of the rings can be predicted with some assurance but the chirality of the donor atom displacements cannot at present be predicted.

Payne^{8,9} has shown for crystals of *trans*-R,R-[Co(3,2,3-tet)(NO₂)₂]Br and *trans*-R,R-[Co(3,2,3-tet)Cl₂]NO₃ that in both cases the inner chelate rings are in the δ conformation and that both outer rings are in chair conformations. However, Payne found that the twist sense of the donor nitrogen atom displacements away from the mean *trans*-CoN₄ plane were opposite in the two complexes (Figure 8). If we assume that the donor atom distortions and the effect of the dissymmetrically disposed groups linking the donor atoms contribute comparable circular dichroism to the d-d bands, then it seems plausible to suppose that while the ring conformations remain essentially constant, mild crystal or solvent perturbations could switch the twist sense of the quasiplanar array of nitrogen atoms and cause much of the variation in circular dichroism observed. We suspect that the variations observed in the solid are principally governed by this effect although the position of the counterion and the other molecules in the unit cell could also have an effect apart from causing distortions of the inner coordination sphere.

In addition to the possible opposing effects engendered by chiral donor atom distortions and the puckered chelate rings, two other effects may also be important in these systems. The first of these is the dissymmetry of the immediate solvation sphere, the molecules of which will tend to pack around the dissymmetric complex ion in a compatible chiral arrangement. While the interaction of the solvent molecules with the d electrons may not have an appreciable effect on the linear absorption, a chiral array of solvent molecules at distances similar to the ligand atoms of the inner sphere could contribute to the circular dichroism as much as the inner sphere. It is perhaps pertinent that, in general, the largest changes are observed in transferring the complexes from dipolar protic solvents (water and alcohols) to dipolar aprotic solvents (DMSO and DMF) and that within each class of solvents the circular dichroism spectra tend to be similar. It is known²⁸ that the analogous *cis*- and *trans*-[Co(en)₂Cl₂]⁺ cations are more strongly solvated in DMF and DMSO than in water and methanol. It is, however, difficult to connect this fact directly with solvation structure except perhaps in a general way. In a protic solvent the hydrogen bonding between the solvent molecules and the amino protons is in competition with the hydrogen-bonded structure of the achiral bulk solvent. These competing structure-inducing forces may tend to produce solvation geometries which are determined by both the chiral cation and the achiral bulk solvent. With aprotic solvents, which only hydrogen bond to the cation, we expect less competition between the structures of the first solvation sphere and the bulk solvent, and hence dipolar aprotic solvents may tend to order their molecules more firmly around the chiral

cations and form more chirally defined solvation spheres. On this basis, solvation in aprotic media would contribute more to the total circular dichroism.

The second effect may occur when the axial ligands can adopt dissymmetric arrangements. Unless we assume completely free rotation, the NO₂⁻, N₃⁻, NCS⁻, and NO₃⁻ ligands can have rotamer conformations which are dissymmetric with respect to the total molecule, and it is possible that as the environment is changed, these could adopt different orientations. We have no real evidence for the participation of this effect except to note that some of the more dramatic variations are in fact observed for these ligands.

Although some fairly large variations in circular dichroism have been observed before,⁶ they have not been as spectacular as the ones described here, and the question arises as to why this system should show them in a pronounced way. Apart from the fact that little systematic work has appeared on this problem, we think it is connected with the small rotational strengths observed in the present system. It may be that the contributions to the circular dichroism from donor atom distortions and dissymmetric solvation are about the same for all conformationally dissymmetric complexes and it is only when the contribution from the chelate ring puckering is of comparable magnitude that these variations are observed to this degree. Indeed we shall describe in the last of this series of papers complexes which have quite large conformationally induced circular dichroism and which show fairly consistent circular dichroism patterns.

8. Experimental Section

The preparation and properties of the complexes are described in the previous paper. Circular dichroism spectra were recorded using a Roussel-Jouan (II) Dichrographe except between 610 and 700 m μ where a modified Durrum-Jasco instrument was used. The preparation of KBr disks is described in a previous paper,⁶ and all disks are 1% in complex and are recorded at a sensitivity of 5 mdeg cm⁻¹. The linear absorption spectra were obtained on a Unicam SP800 spectrophotometer. We have found that, for many of the complexes, trivial changes occur in going from water to methanol and from DMSO to DMF; the greatest changes nearly always are in the transference from one class of solvent to another. Many of the spectra are therefore only given for each class of solvent. We have taken care to check that no isomerization or solvolysis had occurred in any of the solvents and that no substitution had occurred in the KBr disks.

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Registry No. *trans*-R,R-[Co(3,2,3-tet)Cl₂]Cl, 53567-33-2; *trans*-R,R-[Co(3,2,3-tet)Cl₂]BCS, 53625-47-1; *trans*-R,R-[Co(3,2,3-tet)Cl₂]NO₃, 38217-29-7; *trans*-R,R-[Cr(3,2,3-tet)Cl₂]ClO₄, 53625-78-8; *trans*-R,R-[Rh(3,2,3-tet)Cl₂]ClO₄, 53783-40-7; *trans*-R,R-[Co(3,2,3-tet)Br₂]ClO₄, 53783-39-4; *trans*-R,R-[Co(3,2,3-tet)(NO₂)₂]NO₃, 53625-64-2; *trans*-R,R-[Co(3,2,3-tet)(N₃)₂]ClO₄, 36490-58-1; *trans*-R,R-[Co(3,2,3-tet)(OH)₂]⁺, 53834-31-4; *trans*-R,R-[Co(3,2,3-tet)(H₂O)(OH)](ClO₄)₂, 53625-62-0; *trans*-R,R-[Co(3,2,3-tet)(NCS)₂]ClO₄, 53625-66-4; *trans*-R,R-[Co(3,2,3-tet)(NO₂)₂]ClO₄, 53625-75-5; *trans*-R,R-[Co(3,2,3-tet)(NO₂)Br]ClO₄, 53625-71-1; *trans*-R,R-[Co(3,2,3-tet)(NO₂)Cl]ClO₄, 53625-69-7; *trans*-R,R-[Co(3,2,3-tet)(NO₂)(NCS)]ClO₄, 53625-73-3; *trans*-R,R-[Co(3,2,3-tet)(NH₃)₂]Cl₃, 53625-67-5; *trans*-R,R-[Co(3,2,3-tet)(NO₂)₂]Br, 36802-21-8; *trans*-R,R-[Co(3,2,3-tet)(NO₂)₂]ClO₄, 53567-36-5; *trans*-R,R-[Co(3,2,3-tet)(NO₂)₂]BCS, 53625-48-2; *trans*-R,R-[Co(3,2,3-tet)(CN)₂]ClO₄, 53625-51-7.

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 (16) Another source of variation might arise from ion-pair (or aggregate) formation. This seems unlikely since nearly all the salts have perchlorate counterions. We have found no change for perchlorate counterions when the solutions were diluted tenfold. Even the above Cl^- salt in methanol showed the same spectrum when the solutions were diluted from 10^{-1} to 10^{-2} M.
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Chemistry, Stereochemistry, and Molecular Dissymmetry of Metal Complexes Containing a Quadridentate Ligand with Chair Six-Membered Chelate Rings

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The meso and racemic quadridentate ligands produced by the reaction between ethylene dibromide and excess *meso*-2,4-pentanediamine have been separated by means of their cobalt(III) complexes. Both ligands give a rich variety of complexes with varying stereochemistries. Thus it was possible to isolate all three topological isomers, *cis- α* , *cis- β* , and *trans*, of the racemic ligand complexes of cobalt(III) as well as two conformational isomers of each of the *cis- β* and *trans* complexes which differed by either having racemic or meso configurations of the inner nitrogen atoms. Similarly, a *cis- β* isomer with racemic inner nitrogen atoms and the two conformational isomers of the *trans* topology have been isolated with the meso ligand. In general, the racemic ligand has a strong tendency to form *trans* complexes with racemic inner nitrogen atoms, and a large number of complexes with this geometry have been isolated. The meso ligand seems to be less restrictive and forms either *cis- β* or *trans* complexes depending on the conditions of reaction. Conformational arguments are presented in order to rationalize this behavior. Apart from the *trans* complex of the meso ligand with meso inner nitrogen atoms, which is conformationally labile, all the complexes of both the meso and racemic ligand have been obtained in pure optical forms. Their absolute configurations have been assigned from the circular dichroism spectra of their *cis* complexes and through chemical interconversions. The optical, conformational, and topological stability of these complexes are recorded and discussed and their structures have been inferred from a variety of spectroscopic and chemical observations. The ligands appear to be completely stereospecific.

The preceding papers^{1,2} left unresolved the origins of the environmental dependence of the circular dichroism spectra of the *trans*-[Co(3,2,3-tet)XY]ⁿ⁺ complexes. In particular, the possibility that conformational equilibria exist involving the flipping of the terminal six-membered rings between the achiral chair and chiral skew conformations was not excluded. In order to resolve this problem, we have sought to synthesize complexes with stereospecific ligands of the 3,2,3-tet type in which the conformations of the terminal chelate arms would be fixed because of C-alkylation. For this purpose, we have prepared and isolated several isomers of the tetramethylated 3,2,3-ligand, namely, 2,11-diamino-4,9-dimethyl-5,8-diazadodecane ($\text{NH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}(\text{CH}_3)\text{NHCH}_2\text{CH}_2\text{NHCH}(\text{CH}_3)\text{CH}_2\text{CH}(\text{CH}_3)\text{NH}_2$), and in this and subsequent papers we report the preparations, resolutions, and circular dichroism spectra of cobalt(III) complexes with these ligands.

The ligand may exist in six isomeric forms, four racemates and two meso compounds, but because of our synthetic methods using the separate reactions between either the *R,S* or the *R,R:S,S* isomers of the 2,4-diaminopentane molecule and ethylene dibromide we have obtained four of these isomers,

two at a time. This has simplified the experimental problem of separating the isomers while still providing, as we shall show, a series of complexes in which it is probable that all possible conformational forms of the 3,2,3-tet system have been characterized.

The present paper reports the preparation and characterization of cobalt(III) complexes of the two quadridentate ligands derived from (meso) (*R,S*)-2,4-pentanediamine (*R,S*-dmtn). Subsequent papers will deal with the preparations of complexes made from *R,R:S,S*-dmtn as well as the circular dichroism spectra of all the complexes made from all the ligands.

1. The Ligands

Both theoretical^{3,4} and experimental⁵⁻⁷ studies suggest that the most stable conformation of the 1,3-diaminopropane-cobalt(III) chelate ring system is the chair. When such a ring system is substituted as in the case of the *R,S*-dmtn ligand, the system can adopt several conformations of which only one chair conformation can have equatorially disposed methyl groups; the other conformations as well as the inverted chair