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Contribution from the Lash Miller Chemical Laboratories,
University of Toronto, Toronto, Ontario, Canada

Conformational Dissymmetry. Circular Dichroism Spectra of a Series of Complexes Containing a Quadridentate Amine Ligand with Skew Six-Membered Chelate Rings

B. BOSNICH* and J. MacB. HARROWFIELD

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The circular dichroism spectra of an extensive series of complexes of the type *trans*-S,S-[Co(R,R,R,R-sk-3,2,3)XY]$^{n+}$ are recorded and discussed. The systems contain a quadridentate amine ligand with locked skew terminal six-membered chelate rings and the axial ligand fields generated by the X and Y groups span the spectrochemical series. These complexes show d–d circular dichroism patterns which are consistent for nearly all the members of the series and are not very sensitive to the environment. These patterns are quite distinctive and different from those shown by analogous complexes with chair terminal rings. It is concluded that the solvent variations observed in the complexes without conformationally determining substituents were not due to chair–skew conformational changes. The significance of this conclusion in relation to deriving regional rules for conformational isomers is briefly discussed.

We showed in two preceding papers[1,2] that the d–d circular dichroism spectra of complexes of the type *trans*-R,R-[Co(3,2,3-tet)XY]$^{n+}$ displayed dramatic variations in transferring from one medium to another and that these changes were mirrored in the analogous *trans*-S,S-[Co(S,R,R,S-ch-3,2,3)XY]$^{n+}$ complexes, where the terminal six-membered rings are fixed in chair conformations by methyl group substituents. Furthermore, the corresponding members of the two sets of analogous complexes showed similar circular dichroism patterns. This led to the tentative conclusion that the variations in the circular dichroism were due to medium effects and not due to the terminal six-membered rings undergoing chair–skew conformational changes. There were, however, significant differences between the circular dichroism displayed by the two series of compounds and some doubt remained about the general validity of the assertion of conformational rigidity. In addition, the nature of the circular dichroism displayed by analogous systems with skew terminal rings was not known and thus the variations that might occur if the terminal rings were flexible could not be anticipated.

In the preceding paper[3] we described a series of complexes containing a quadridentate amine ligand with skew terminal six-membered chelate rings. This paper describes their circular dichroism spectra; we will show that these complexes give circular dichroism spectra which are different from those of the chair analogs, that they are the same, for a given complex, from one medium to another, and that they show consistent patterns.

Except for two complexes of the analogous meso ligand, R,R,S,S-sk-3,2,3, all the compounds described here are of the type *trans*-S,S-[Co(R,R,R,R-sk-3,2,3)XY]$^{n+}$ and their absolute configurations are known with certainty.[3] The absolute configuration and conformation of these complexes are shown in Figure 1. The following discussion presupposes the spectroscopic details and considerations given in the second paper[1] of this series. We proceed by comparing the spectra of the *trans*-dichloro complexes derived from the meso and racemic ligands.

1. Dichloro Complexes

Figure 2 shows the spectra of the complexes *trans*-S,S-[Co(R,R,R,R-sk-3,2,3)Cl_2]ClO_4, derived from the optically active ligand, and *trans*-S,S-[Co(R,R,S,S-sk-3,2,3)Cl_2]ClO_4, derived from the meso ligand. The absolute configuration of the latter was derived on empirical grounds;[3] the conformation of one of the terminal rings is not known although we presented evidence[3] which may suggest that it is in a chair conformation with an axial methyl group (Figure 2). It could, however, be in a distorted skew-boat conformation but it is highly probable[3] that the other terminal ring is in a skew conformation.

Both complexes show similar circular dichroism spectra in methanol and DMSO and in the solid state. Unlike the analogs with chair terminal rings, both show strong $^1A_{2g}$ bands. The ^1E_g bands are weaker than the $^1A_{2g}$ band and opposite in sign. It will also be noted that the positive circular dichroism absorption at around 26,000 cm^{-1}, corresponding to the components of the $^1A_{1g} \rightarrow {}^1T_{2g}$ transition, are of the same order of magnitude as the $^1T_{1g}$ components. These spectra are remarkably insensitive to their environment except for the case of the complex derived from the meso ligand which shows a splitting of the ^1E_g band in the solid state, a splitting which was not observed in solutions. In view of the strained nature of one of the terminal rings, it is possible that conformational changes occur in this ring in going from solution to the solid. Thus it appears that the introduction of at least one skew terminal ring to these quadridentate ligand complexes has a marked and distinctive effect on their circular dichroism. These patterns are generally repeated for the other complexes.

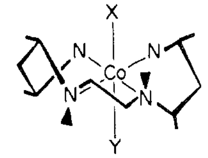

Figure 1. The conformations of the rings in the *trans*-S,S-[Co(R,R,R,R-sk-3,2,3)XY]$^{n+}$ complexes. The two terminal skew rings are in λ conformations; the central ring is δ.

2. Complexes with Weak Axial Fields

Figure 3 shows the spectra of the complexes *trans*-S,S-[Co(R,R,R,R-sk-3,2,3)$(N_3)_2$]ClO_4 and *trans*-S,S-[Co(R,R,R,R-sk-3,2,3)$(NO_3)_2$]ClO_4. The diazido species shows a strong negative $^1A_{2g}$ band and a weaker positive ^1E_g transition in all media, which is completely analogous to the pattern observed for the dichloro analog. In transferring from water to DMSO large changes in the circular dichroism occur, particularly for the ^1E_g band. These changes are as large in magnitude as those encountered for the analogous complexes with chair terminal rings. In this case, however, the basic pattern is preserved in all media.

The dinitrato complex is only stable in methanol solution; in other common solubilizing solvents extensive solvolysis occurs. As for the other complexes the $^1A_{2g}$ band is negative but, unlike all the other complexes of this series, the ^1E_g band shows a couplet in both the solid and the solution. The reason for the appearance of a ^1E_g couplet in this case is not clear, although it may imply that, in fact, all the complexes of the present series have plus–minus couplets for the ^1E_g band but that, in the other cases, the positive component dominates. The other feature of the dinitrato spectrum which is of interest is that the $^1T_{2g}$ manifold carries very weak circular dichroism, unlike the case of the dichloro complex.

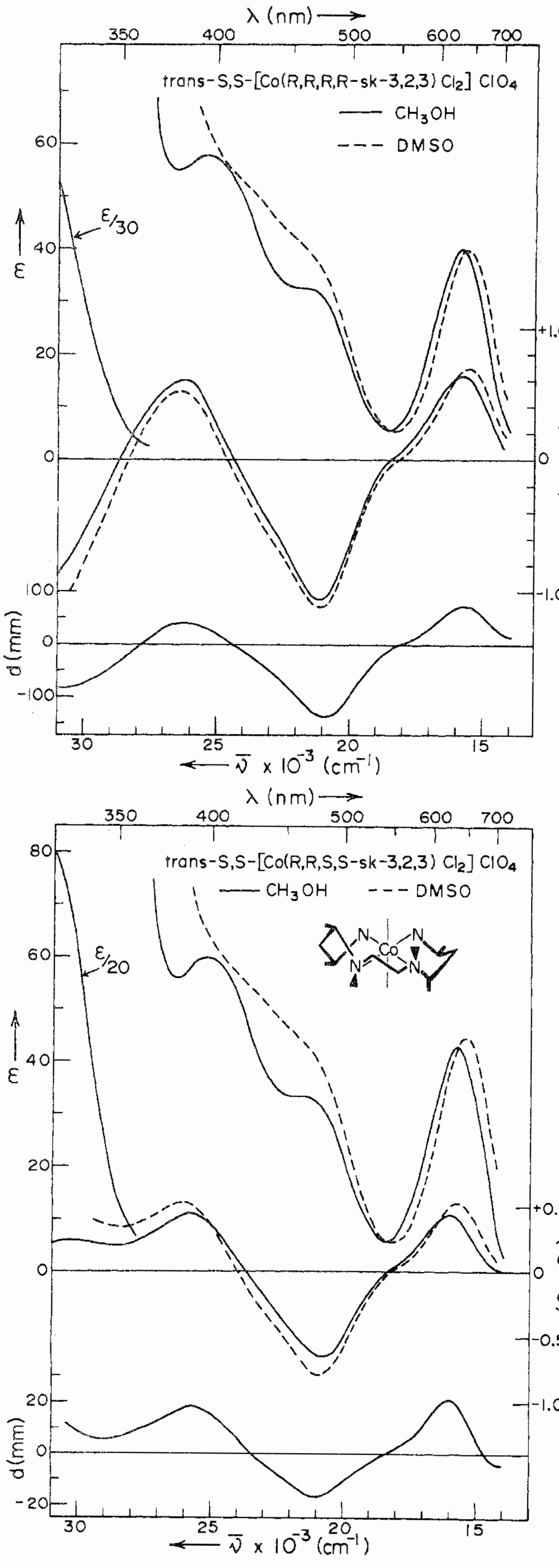

Figure 2.

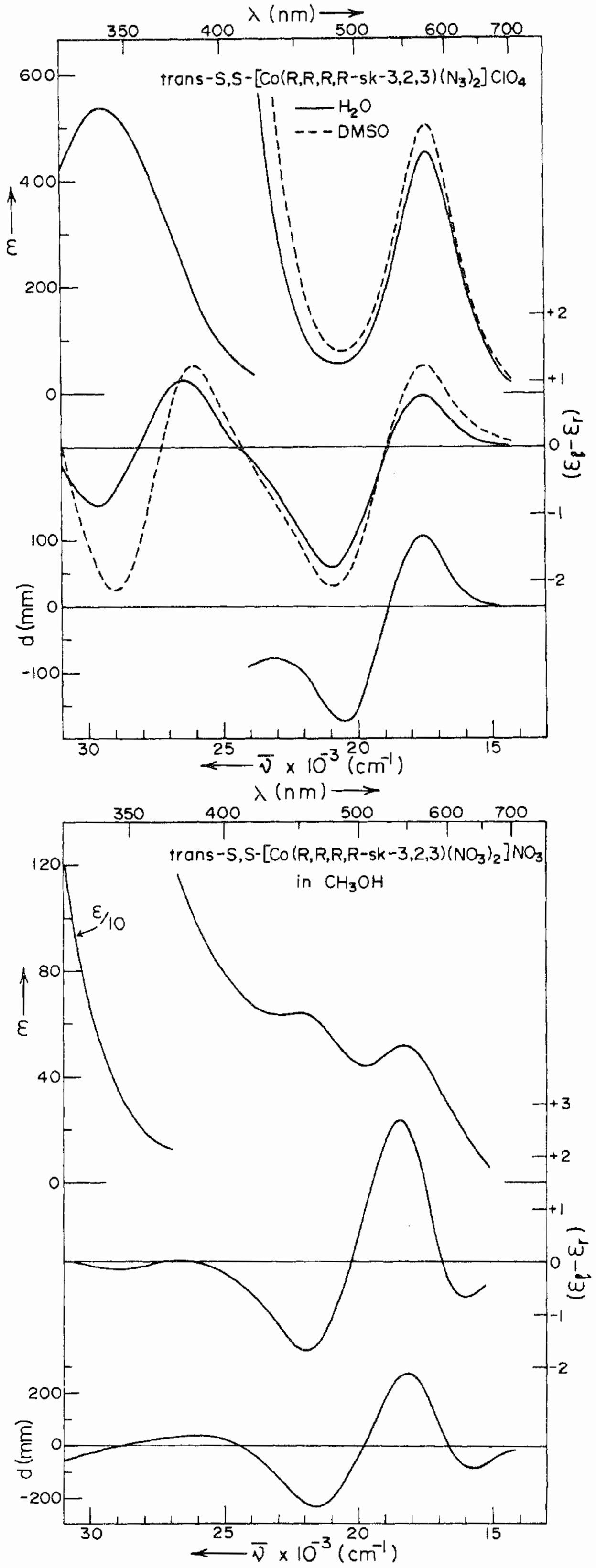

Figure 3.

3. Complexes with Medium-Strength Axial Fields

Figure 4 shows the absorption and associated circular dichroism spectra of the three complexes *trans*-*S*,*S*-[Co(*R*,*R*,*R*,*R*-sk-3,2,3)(NO_2)Cl]ClO_4, *trans*-*S*,*S*-[Co(*R*,*R*,*R*,*R*-sk-3,2,3)(NO_2)N_3]ClO_4, and *trans*-*S*,*S*-[Co(*R*,*R*,*R*,*R*-sk-3,2,3)$(NCS)_2$]ClO_4. The first complex solvolyzes rapidly in water and its spectrum in methanol solution is shown. All three spectra are similar to each other and to the other spectra shown by this series of complexes; all three show a strong negative $^1A_{2g}$ band and a weaker positive ^1E_g transition. It is among these three complexes that some of the largest variations in circular dichroism are observed for the complexes with chair terminal rings. Variations of a similar magnitude are observed here, for example, the variations of the ^1E_g band of the nitroazido species, but the basic patterns are retained.

4. Complexes with Equivalent Axial and Equatorial Fields

The *trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)(NO_2)NCS]ClO_4 and *trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)(NH_3)$_2$]Cl_3 complexes (Figure 5) have nearly equivalent in-plane and axial crystal fields. Previously[1,2] we assigned the higher energy component of the $^1T_{1g}$ manifold to the $^1A_{2g}$ transition for the nitroisothiocyanato complexes although the difference in energy between the $^1A_{2g}$ and ^1E_g components is very small. This earlier assignment, however, tends to be supported by the circular dichroism spectra observed for the present complex provided we assume that, in conformity with the circular dichroism of the other complexes of the present series, the $^1A_{2g}$ band will be negative and the ^1E_g band positive.

We carry over this assumption of circular dichroism sign patterns in assigning the components of the $^1T_{1g}$ manifold of the diammine complex where the positive and negative circular dichroism components of the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition are assigned to the ^1E_g and $^1A_{2g}$ components, respectively. In going to the solid the $^1A_{2g}$ band becomes relatively much weaker compared to the ^1E_g band which shifts slightly to higher energies compared to its position in solution. This may be due to a decrease in splitting between the $^1A_{2g}$ and ^1E_g levels in going from solution to the solid state.

5. Complexes with Strong Axial Fields

Figure 6 shows the spectra of *trans-S,S*-[Co(*R,R,R,R*-sk-3,2,3)(NO_2)$_2$]ClO_4 and *trans-S,S*-[Co(*R,R,S,S*-sk-3,2,3)(NO_2)$_2$]NO_3. The latter is derived from the meso ligand and may have the conformation[3] shown in Figure 2 for the dichloro analog. These are the only complexes of this series which show inconsistent patterns for their circular dichroism spectra. The complex derived from the optically active ligand (top diagram) shows a very weak positive $^1A_{2g}$ band and a dominant negative ^1E_g band in DMSO solution but only the ^1E_g band of increased intensity is observed in water solution. In transferring to the solid, the ^1E_g band reverses in sign. To lower energies, a weaker positive shoulder around 20,000 cm^{-1} is observed and probably represents the $^1A_{2g}$ band. A similar result obtains for the corresponding complex derived from the meso ligand where only a negative ^1E_g band is observed in water solution, but, in the solid, both the ^1E_g and $^1A_{2g}$ bands become positive.

The *trans*-dicyano complex, Figure 7, however, shows the expected pattern, namely, a negative $^1A_{2g}$ band and positive ^1E_g band in all media. The only significant difference between it and the majority of the other complexes is that in all media the $^1A_{2g}$ band is weaker than the ^1E_g band.

6. Discussion

The consistency of the circular dichroism patterns shown by this series of complexes compared to the generally miscellaneous patterns observed for the other two series of complexes raises the question as to the reasons for this difference. The first obvious difference is that the circular dichroism intensities, at least for the $^1A_{2g}$ bands, of the present systems are generally 2 or 3 times larger than the intensities observed for the other two series of complexes. Thus even if environmental variations of about the same magnitude occurred in all three systems, the weaker spectra would appear drastically altered, whereas in the more intense spectra, these variations would appear only as modulations of the basic patterns. An inspection of the three sets of spectra reveals that the environmental variations are roughly the same in many of the cases. There are, however, among the circular dichroism spectra of the other two series, variations which are so large

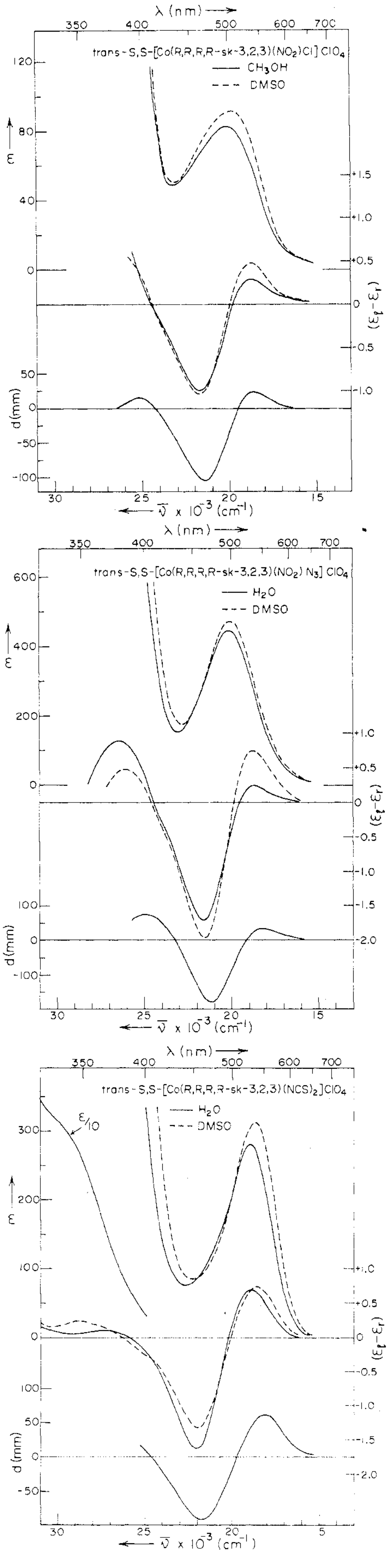

Figure 4.

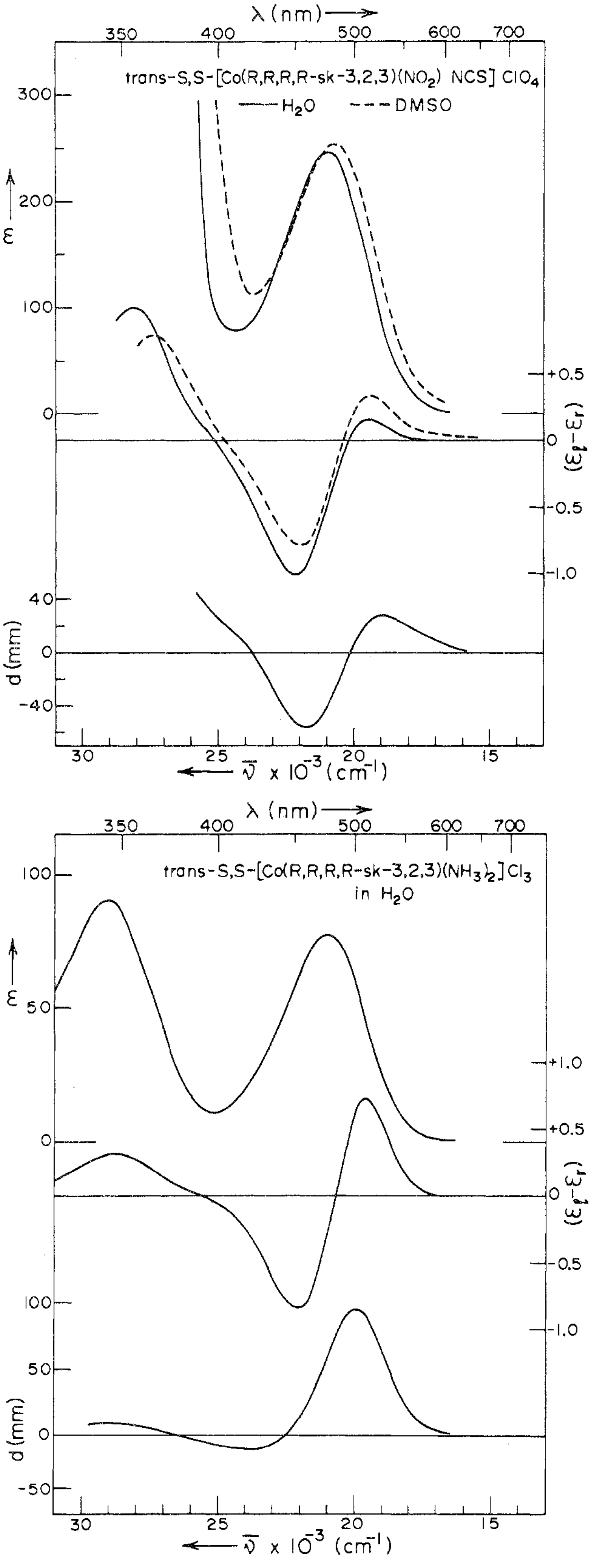

Figure 5.

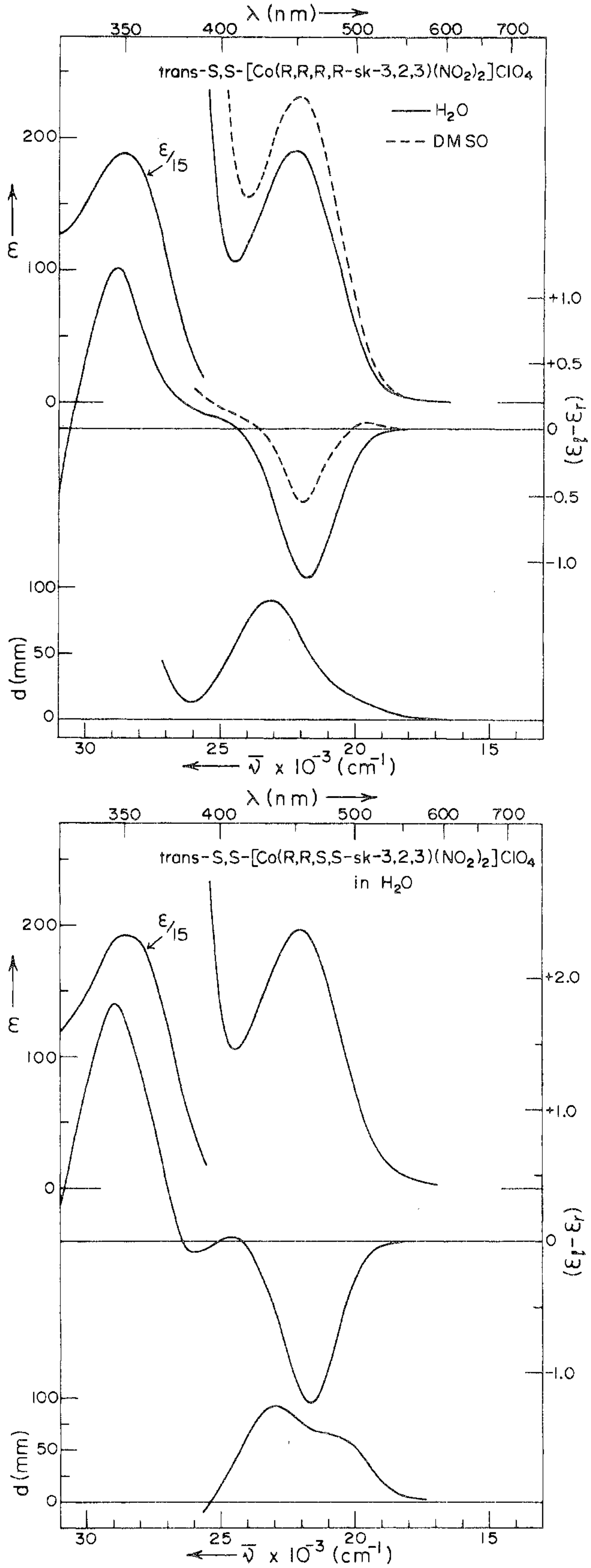

Figure 6.

as to suggest that, in general, these systems with chair terminal rings are more susceptible to environmental influences than the analogous systems with skew terminal rings. Molecular models indicate that the trans complexes with chair terminal rings have a more open structure where the central cobalt atom is more exposed than for the case of the skew ring systems which tend to "insulate" the cobalt atom. Thus, in the former, solvent molecules can arrange themselves more closely to the central metal atom than in the latter and hence any dissymmetric perturbation emanating from the solvent sphere is expected to be more effective in the chair systems than in those with skew terminal rings. Another potential source of dis-

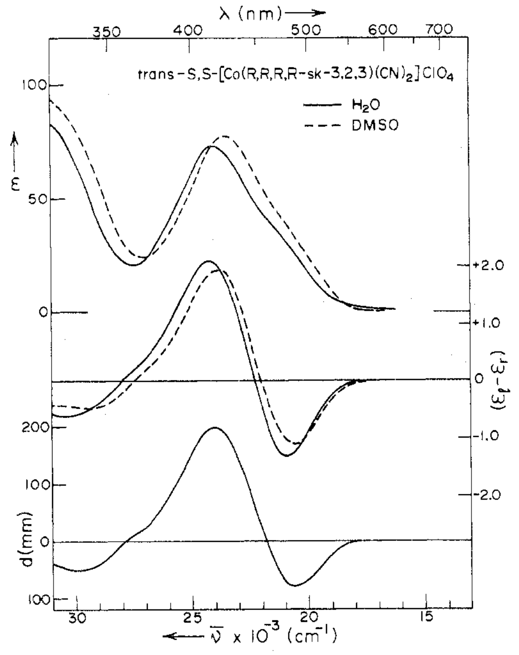

Figure 7.

symmetry, namely, the orientations of nonaxially symmetrical X and Y groups,[1] may also be affected by the surrounding rings but in the absence of conformational energy calculations it is difficult to be precise on the matter. It is possible that this effect is responsible for the variations observed in the circular dichroism spectra of the dinitro complexes of the present series but if this were so, it is difficult to understand why similar variations do not occur with, for example, the nitro–X complexes.

We have shown elsewhere[4] that skew six-membered rings show much stronger circular dichroism in the $^1A_{2g}$ band than the corresponding five-membered ring systems in conformationally dissymmetric tetragonal cobalt(III) complexes. In the present series, where the ring sequence is λ, δ, λ (Figure 1), the spectra are very similar in both sign pattern and intensity to the corresponding circular dichroism spectra shown by the *trans*-[Co(*R*,*R*-dmtn)XY]$^{n+}$ complexes[5] (*R*,*R*-dmtn = (*R*,*R*)-2,4-diaminopentane). This suggests that the circular dichroism in the present systems is dominated by the contributions of the terminal skew rings. This must certainly be true for the $^1A_{2g}$ band which generally showed very weak circular dichroism in the previous two series of complexes[1,2] where the primary source of dissymmetry was the central five-membered ring. Even the *trans*-*S*,*S*-[Co(*R*,*R*,*S*,*S*-sk-3,2,3)Cl$_2$]$^+$ with only one skew ring shows a strong $^1A_{2g}$ band.

One of the two major objects of this series of papers was to examine critically the regional rules that have been proposed for correlating circular dichroism and absolute configuration of conformationally dissymmetric complexes.[4,6,7] In particular we were interested[6] in whether the circular dichroism spectra shown by the $^1T_{1g}$ transition were dependent on the relative strengths of the axial and equatorial ligand fields. No general statements can be made about the circular dichroism of the first two series of complexes[1,2] because of their high sensitivity to the environment which was also observed in the $^1A_{2g}$ bands of the classic *trans*-bis(diamine)cobalt(III) complexes with five-membered chelate rings.[4] The systems with skew six-membered chelate rings, in the main, show consistent patterns which are not greatly influenced by the relative strengths of the axial and equatorial fields. Those variations in intensity which do occur probably in most cases could be explained by a mixing mechanism involving charge-transfer states. As far as the application of the proposed[4,6,7] regional rules is concerned, any one of these accommodates the circular dichroism spectra of the systems with skew six-membered rings provided the sign of the $^1A_{2g}$ band is taken. In fact all that is required is that an octahedral edge be divided into a quadrant (+ or $-XY$) and that the adjoining edges of the equatorial plane be similarly divided but with alternating phase relationships.[4] The use of a "net" sign[6] for the $^1T_{1g}$ manifold nearly works as well.

The other major object of this series of papers concerned the conformational stability of the *trans*-[Co(3,2,3-tet)XY]$^{n+}$ complexes. We have shown[2] that the systems with fixed chair terminal rings exhibit circular dichroism spectra which are as sensitive to the environment as the unsubstituted analogs. This established that large solvent variations could occur without conformational changes but did not determine what changes in circular dichroism would be expected if conformational changes did occur. The only reasonable conformational flexibility[8,9] would involve chair to skew transformations but the circular dichroism spectra of the present series are so different in structure from the corresponding members of the other two series in any environment as to preclude this possibility. Even when the CD structures are similar, as in, for example, the *trans*-nitroisothiocyanato complexes in DMF or DMSO, the signs of the corresponding components are reversed for the chair and skew systems. We, of course, recognize that there may be distortions of the basic chair and skew rings in changing environments but the conclusion that there is no flipping between these canonical conformations in the *trans*-[Co(3,2,3-tet)XY]$^{n+}$ complexes seems the only rational conclusion to be drawn from the extensive evidence.

The implications of this conclusion go to the very essence of much of the effort in this area and elicit extreme caution in discussing the d–d circular dichroism spectra of conformationally dissymmetric complexes. We think that planar amino acid complexes are particularly likely to be susceptible to the ambiguities encountered here. Except for narrowly specified and thoroughly investigated systems, the prospect of developing reliable regional rules for conformationally dissymmetric complexes on the basis of their d–d circular dichroism spectra appears bleak indeed.

7. Experimental Section

The preparations and resolutions of these complexes are described in the preceding paper[3] and the same instrumentation was used. Due care was taken with problems of solvolysis, isomerization, and substitution. The results here are free of these complications.

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Registry No. *trans*-*S*,*S*-[Co(*R*,*R*,*R*,*R*-sk-3,2,3)Cl$_2$]ClO$_4$, 53833-96-8; *trans*-*S*,*S*-[Co(*R*,*R*,*S*,*S*-sk-3,2,3)Cl$_2$]ClO$_4$, 53834-06-3; *trans*-*S*,*S*-[Co(*R*,*R*,*R*,*R*-sk-3,2,3)(N$_3$)$_2$]ClO$_4$, 36535-50-9; *trans*-*S*,*S*-[Co(*R*,*R*,*R*,*R*-sk-3,2,3)(NO$_3$)$_2$]NO$_3$, 53860-99-4; *trans*-*S*,*S*-[Co(*R*,*R*,*R*,*R*-sk-3,2,3)(NO$_2$)Cl]ClO$_4$, 53783-31-6; *trans*-*S*,*S*-[Co(*R*,*R*,*R*,*R*-sk-3,2,3)(NO$_2$)N$_3$]ClO$_4$, 53783-33-8; *trans*-*S*,*S*-[Co(*R*,*R*,*R*,*R*-sk-3,2,3)(NCS)$_2$]ClO$_4$, 53783-26-9; *trans*-*S*,*S*-[Co(*R*,*R*,*R*,*R*-sk-3,2,3)(NO$_2$)(NCS)]ClO$_4$, 53783-35-0; *trans*-*S*,*S*-[Co(*R*,*R*,*R*,*R*-sk-3,2,3)(NH$_3$)$_2$]Cl$_3$, 53783-29-2; *trans*-*S*,*S*-[Co(*R*,*R*,*R*,*R*-sk-3,2,3)(NO$_2$)$_2$]ClO$_4$, 53833-98-0; *trans*-*S*,*S*-[Co(*R*,*R*,*S*,*S*-sk-3,2,3)(NO$_2$)$_2$]ClO$_4$, 53834-08-5; *trans*-*S*,*S*-[Co(*R*,*R*,*R*,*R*-sk-3,2,3)(CN)$_2$]ClO$_4$, 53783-28-1.

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