

cis-β-S,S-[Co(*S,R,R,S*-ch-3,2,3)CO₃]ClO₄, 53834-25-6; (–)-Δ-*cis-α-R,R*-[Co(*S,R,R,S*-ch-3,2,3)Cl₂]Cl, 53834-26-7; Δ-*cis-β-R,R*-[Co(*S,R,R,S*-ch-3,2,3)Cl₂]ClO₄, 53834-28-9; *trans-R,S*-[Co(*S,R,R,S*-ch-3,2,3)Cl₂]ClO₄, 53834-30-3; (–)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)(N₃)₂]ClO₄, 36464-25-2; (–)₄₃₆-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)(NCS)₂]ClO₄, 53860-91-6; (–)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)(NO₃)₂]NO₃, 53783-42-9; (–)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)(CN)₂]ClO₄, 53834-34-7; (–)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)(NH₃)₂]Cl₃, 53834-35-8; (–)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)(NO₂)Cl]ClO₄, 53834-39-2; (+)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)(NO₂)N₃]ClO₄, 53834-37-0; (–)-*trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)(NO₂)(NCS)]ClO₄, 53860-93-8; *trans-R,S*-[Co(*R,S,R,S*-ch-3,2,3)Cl₂]Cl, 53834-40-5; *cis-β-R,R,S*-[Co(*R,S,R,S*-ch-3,2,3)CO₃]Cl, 53834-46-1; (+)-Δ-*cis-β-R,R*-[Co(*R,S,R,S*-ch-3,2,3)CO₃]BCS, 53834-48-3; (+)-Δ-*cis-β-R,R*-[Co(*R,S,R,S*-ch-3,2,3)CO₃]BPh₄, 53860-87-0; (–)₅₄₆-*trans-S,S*-[Co(*R,S,R,S*-ch-3,2,3)Cl₂]ClO₄, 53834-42-7; (–)-Δ-*cis-β-R,R*-[Co(*R,S,R,S*-ch-3,2,3)Cl₂]Cl, 53834-43-8; (+)-Δ-*cis-β-R,R*-[Co(*R,S,R,S*-ch-3,2,3)(N₃)₂]NO₃, 53834-45-0; ch-3,2,3,4HCl, 53834-32-5.

References and Notes

- (1) B. Bosnich, J. MacB. Harrowfield, and H. Boucher, *Inorg. Chem.*, **14**, 815 (1975).
- (2) B. Bosnich and J. MacB. Harrowfield, *Inorg. Chem.*, **14**, 828 (1975).
- (3) M. R. Snow, *J. Amer. Chem. Soc.*, **92**, 3610 (1970).
- (4) S. R. Niketic and F. Woldbye, *Acta Chem. Scand.*, **27**, 621 (1973).
- (5) K. Matsumoto, M. Yonezawa, H. Kuroya, H. Kawaguchi, and S. Kawaguchi, *Bull. Chem. Soc. Jap.*, **43**, 1269 (1970).
- (6) H. Kawaguchi, K. Matsumoto, H. Kuroya, and S. Kawaguchi, *Chem. Lett.*, 125 (1972).
- (7) Y. Saito, T. Nomura, and F. Marumo, *Bull. Chem. Soc. Jap.*, **41**, 530 (1968).
- (8) N. C. Payne, *Inorg. Chem.*, **11**, 1376 (1972).
- (9) N. C. Payne, *Inorg. Chem.*, **12**, 1151 (1973).
- (10) B. Bosnich, M. L. Tobe, and G. A. Webb, *Inorg. Chem.*, **4**, 1109 (1965). [Note: The designations, *R* and *S*, for the coordinated *S,R,R,S*-ch-3,2,3 and 3,2,3-tet ligands are reversed because of the CH₃ groups.]
- (11) L. J. De Hayes, M. Parris, and D. H. Busch, *Chem. Commun.*, 1398 (1971); J. Cragel and G. R. Brubaker, *Inorg. Chem.*, **11**, 303 (1972); L. J. De Hayes and D. H. Busch, *ibid.*, **12**, 2010 (1973).
- (12) The introduction of methyl groups at the terminal arms of the *trans-R,R*-[Co(3,2,3-tet)X₂]ⁿ⁺ systems requires the absolute configurations of the inner nitrogen atoms to be designated *S*, even though the inner ring conformation remains *δ*. The *δ* conformation is compatible only with the *S,R,R,S*-ch-3,2,3 absolute configuration of the ligand (Figure 2).
- (13) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **4**, 45 (1965).
- (14) M. Saburi and S. Yoshikawa, *Bull. Chem. Soc. Jap.*, **45**, 806 (1972).
- (15) G. R. Brubaker, D. P. Schaefer, J. H. Worrell, and J. I. Legg, *Coord. Chem. Rev.*, **7**, 161 (1971), and references therein.

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 Chair Six-Membered Chelate Rings

B. BOSNICH* and J. MacB. HARROWFIELD

Received July 5, 1974

AIC40438M

The circular dichroism spectra of a series of complexes of the type *trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)XY]ⁿ⁺ where *S,R,R,S*-ch-3,2,3 is a stereospecific quadridentate ligand, the substituents of which fix the terminal six-membered chelate rings in chair conformations, are recorded. The X and Y ligands span the spectrochemical series. Despite the fixed conformations of the rings, large solvent variations are observed in the circular dichroism patterns of these complexes. These variations are very similar to those found for the corresponding *trans-R,R*-[Co(3,2,3-tet)XY]ⁿ⁺ complexes where it might have been assumed that the circular dichroism changes were due to conformational instability. The results described for the *trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)XY]ⁿ⁺ system strongly suggest that this is not the case and that the variations are due to other effects engendered by the medium.

In a previous paper¹ we showed that complexes of the type *trans-R,R*-[Co(3,2,3-tet)XY]ⁿ⁺ gave circular dichroism spectra which were extremely sensitive to the environment. So gross and spectacular were some of these effects, that a genuine case could be made which inferred changes in the conformations from one environment to another. More particularly, some of the observations could be construed as being a result of chair-skew conformational changes of the terminal six-membered chelate rings. We have sought to resolve this inference by preparing complexes of the 3,2,3-tet type where, by methyl substitution of the terminal rings, the conformations would be fixed in either the chair² or skew geometries. This paper presents the circular dichroism spectra of an analogous series of complexes where the terminal rings are fixed in chair conformations; a subsequent paper deals with fixed skew terminal rings.

Except for two dichloro complexes, all the complexes derived from the active *S,R,R,S*-ch-3,2,3 ligand have the structure and absolute configuration *trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)XY]ⁿ⁺ (Figure 1). With this absolute configuration, the inner five-membered ring is *δ* and with the given sequence of chiral centers, both terminal rings are in chair conformations. Apart from the methyl groups, the complexes are superimposable on

the *trans-R,R*-[Co(3,2,3-tet)XY]ⁿ⁺ complexes discussed previously.¹ The analogy is therefore complete except for a presumably small vicinal effect due to the asymmetric carbon atoms and that which distinguishes this system from the unsubstituted analog, a certainty about the chair conformations of the terminal chelate rings. The absolute configurations of these complexes of the racemic ligand are derived on fairly convincing empirical grounds² and are almost certainly correct but are not proven beyond doubt. What is certain, however, is that they all have the same absolute configurations;² and since the primary object of this paper is to begin to resolve the issue of conformational lability in inducing the circular dichroism changes in the 3,2,3-tet complexes, the argument does not hinge on a certain knowledge of the absolute configuration.

In a preceding paper,¹ we gave a fairly comprehensive introduction to and analysis of the circular dichroism spectra of these types of complexes. We will not repeat these here. The material and methodology of the preceding paper are assumed to serve as an introduction to this and the subsequent paper on systems with skew rings. We begin slightly obliquely by describing the spectra of three *trans*-dichloro complexes which have various conformations of the terminal rings because

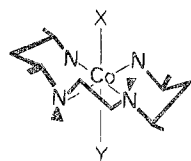


Figure 1. The conformational structure and absolute configuration of $\text{trans-}S,S\text{-[Co(S,R,R,S-ch-3,2,3)XY]}^{2+}$ complexes.

of either the structure of the ligand or its inner nitrogen configurations.

1. *trans*-Dichloro Complexes of the Racemic and Meso Ligands

Figure 2 shows the absorption and circular dichroism spectra of the $\text{trans-}S,S\text{-[Co(S,R,R,S-ch-3,2,3)Cl}_2\text{]}^+$ and the $\text{trans-}R,S\text{-[Co(S,R,R,S-ch-3,2,3)Cl}_2\text{]}^+$ ions, both of which are derived from the active ligand, as well as the complex ion derived from the meso ligand $\text{trans-}S,S\text{-[Co(R,S,R,S-ch-3,2,3)Cl}_2\text{]}^+$. The suggested conformations of the ligands attached to the complexes are shown in the diagrams. The one given for the $\text{trans-}S,S\text{-[Co(S,R,R,S-ch-3,2,3)Cl}_2\text{]}^+$ ion is undoubtedly correct; the rings shown on the right for the two other complexes are drawn in boat conformations wherein the methyl groups adopt pseudoequatorial dispositions.² We do not know what precise conformations these rings will adopt although we consider it probable that they will adjust to a conformation somewhere between a boat and a skew. With the drawn δ conformation of the inner ring, the six-membered ring shown on the left in both of the latter complexes can adopt a chair conformation wherein the methyl groups are equatorially disposed.

The $\text{trans-}S,S\text{-[Co(S,R,R,S-ch-3,2,3)Cl}_2\text{]}^+$ ion, which is totally analogous to the $\text{trans-}R,R\text{-[Co(3,2,3-tet)Cl}_2\text{]}^+$ complex, shows circular dichroism which is very similar to that of the latter.¹ There is, however, in this as well as in the 3,2,3-tet complex a puzzling feature in the circular dichroism between 18,000 and 23,000 cm^{-1} . In the region 14,000–23,000 cm^{-1} only the three components of the ${}^1T_{1g}$ manifold should occur and yet four components are clearly seen in the circular dichroism in methanol solution. Previously,¹ we ascribed the negative band at 18,500 cm^{-1} to a spin-forbidden excitation by analogy with the rhodium complex which also showed extra features in the equivalent spectroscopic region. This explanation may also be correct here but it could conceivably arise from solvation effects which we discuss later. As in the 3,2,3-tet system, gross changes occur in going to the solid, and it is of interest that the ClO_4^- salt gives exceedingly weak circular dichroism relative to most other solid-state spectra of this series and the 1E_g band is very weak relative to that of the Cl^- salt. This tends to support our earlier suggestion¹ that the circular dichroism in these complexes is the resultant of two opposing sources of asymmetry which are nearly in balance.

We had only sufficient of the optically active $\text{trans-}R,S\text{-[Co(S,R,R,S-ch-3,2,3)Cl}_2\text{]ClO}_4$ complex to run the solid-state circular dichroism but as can be seen a quite strong circular dichroism is observed throughout the visible region despite the fact that the inner nitrogen atoms are in a meso configuration. In the solid the chelate rings presumably will be in a fixed conformational chirality which is governed by the chirality of the active ligand and crystal packing forces.

The other complex $\text{trans-}S,S\text{-[Co(R,S,R,S-ch-3,2,3)Cl}_2\text{]ClO}_4$ is the obverse of the one just discussed in the sense that one complex is optically active only because of the presence of a chiral ligand while in the other, the ligand is meso and the chirality is fixed by the dissymmetry of the inner nitrogen atoms. The meso ligand complex shows strong circular dichroism in both the solid and solution and the two reproduce

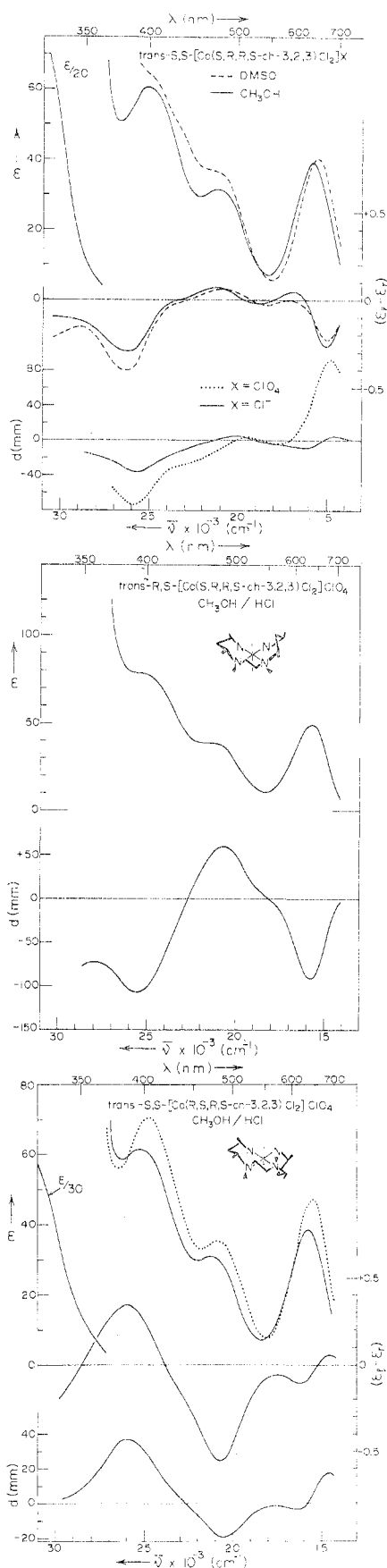


Figure 2. Absorption and circular dichroism spectra of $\text{trans-}S,S\text{-[Co(S,R,R,S-ch-3,2,3)Cl}_2\text{]}^+$ (top), $\text{trans-}R,S\text{-[Co(S,R,R,S-ch-3,2,3)Cl}_2\text{]}^+$ (middle), and $\text{trans-}S,S\text{-[Co(R,S,R,S-ch-3,2,3)Cl}_2\text{]}^+$ (bottom). Diagrams shown are drawn with the right-hand six-membered ring in a boat conformation; they are probably in distorted skew-boat conformations. Absorption spectrum of $\text{trans-}R,S\text{-[Co(R,S,R,S-ch-3,2,3)Cl}_2\text{]Cl}$ shown as the dotted curve in bottom diagram.

each other. The very strong ${}^1A_{2g}$ bands shown by these two complexes with strained-ring systems and the reproducibility of the solid and the solution spectra of one of these are reminiscent of the spectra we describe for the analogous systems with skew terminal rings. This suggests that the strained six-membered ring in both of these complexes is in a quasiskew conformation, the chirality of which is determined by the chiral centers of the ligand in one case and by the inner nitrogen atom chirality in the other.

2. Complexes with Weak Axial Fields

Figure 3 shows the spectra of the *trans*-*S,S*-[Co(*S,R,R,S*-*S*-ch-3,2,3)(NO₃)₂]NO₃ and *trans*-*S,S*-[Co(*S,R,R,S*-*S*-ch-3,2,3)(N₃)₂]ClO₄ complexes. The dinitrato complex is only stable in methanol; in other common solubilizing solvents extensive solvolysis occurs but the circular dichroism is remarkably similar to the 3,2,3-tet analog. The plus-minus couplet under the 1E_g band is again observed in the reverse sense to that of the corresponding dichloro complexes, the only difference being the presence of a slightly positive ${}^1A_{2g}$ band both in solution and in the solid state.

Similarly the diazido complex shows circular dichroism in the solid and in DMSO which is almost identical with that of the 3,2,3-tet analog. The circular dichroism in water, however, is somewhat different and presents a similar problem in interpretation as that mentioned for the dichloro system. We discuss this later; but it is apparent that this system, with fixed ring conformations, shows the same type of variations, which are of the same order of magnitude as those encountered for the corresponding 3,2,3-tet complex.

3. Complexes with Medium-Strength Axial Fields

In Figure 4 the spectra of *trans*-*S,S*-[Co(*S,R,R,S*-*S*-ch-3,2,3)(NCS)₂]ClO₄, *trans*-*S,S*-[Co(*S,R,R,S*-*S*-ch-3,2,3)(NO₂-N₃)ClO₄, and *trans*-*S,S*-[Co(*S,R,R,S*-*S*-ch-3,2,3)(NO₂)Cl]ClO₄ are shown. All these spectra are very similar to the corresponding 3,2,3-tet complexes in their variations from one environment to another and in their form for a given environment. There are some differences, however, and although, for the case of the diisothiocyanato complex, the DMSO spectra of the two complexes are nearly the same, the ${}^1A_{2g}$ band of the 3,2,3-tet analog becomes negative in water but remains positive in water for the present system.

The nitroazido complex also shows some differences; whereas the spectra of this and the unsubstituted analog are almost identical in water, the two spectra differ in DMSO where, for the 3,2,3-tet complex, a couplet is observed for the 1E_g band, while only a plain negative band is observed for the present system. The greatest difference, however, is in the solid-state spectrum which in the present system displays all three components of the ${}^1T_{1g}$ manifold, whereas in the other, only two of the components are resolved.

The only significant difference between the two nitrochloro complexes is that the substituted analog in DMSO shows a positive shoulder at 24,000 cm⁻¹. This circular dichroism band probably represents the higher energy wing of the ${}^1A_{2g}$ component which was observed as a weak positive band heavily overlapped by a single negative 1E_g band component in the 3,2,3-tet complex spectrum in DMF.

4. Complexes with Equivalent Axial and Equatorial Fields

The complexes *trans*-*S,S*-[Co(*S,R,R,S*-*S*-ch-3,2,3)(NH₃)₂]Cl₃ and *trans*-*S,S*-[Co(*S,R,R,S*-*S*-ch-3,2,3)(NO₂)NCS]ClO₄ have nearly equivalent axial and in-plane crystal fields; their spectra are shown in Figure 5. The nitroisothiocyanato complexes of the two series exhibit similar spectra in solution, but in the solid state, the 3,2,3-tet analog shows a minus-plus couplet whereas the present system shows two negative bands under the ${}^1T_{1g}$ manifold.

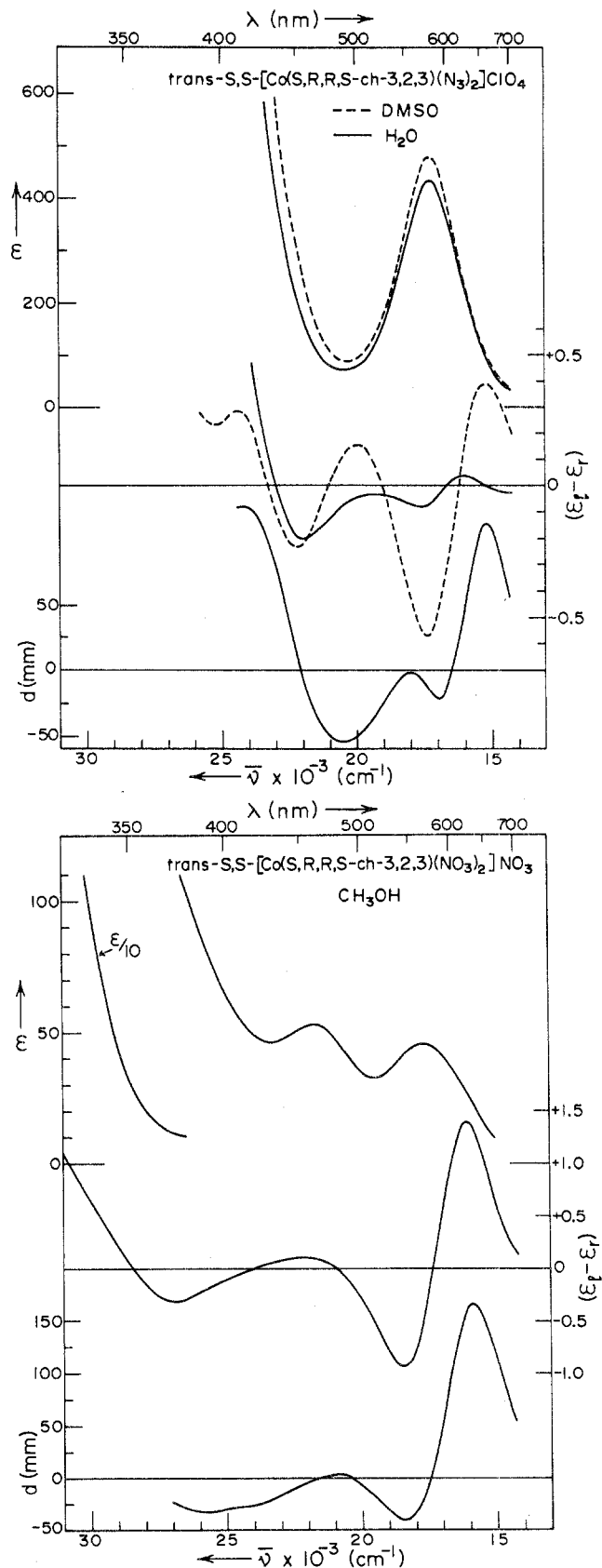


Figure 3.

The diammine complex is quite different from the unsubstituted analog in its solid circular dichroism. The present system shows a rather flat positive feature in the range 23,000–26,000 cm⁻¹ (which is not an artifact) and since this region is almost devoid of linear absorption, it seems plausible to assign it to the resultant of the wings of positive circular

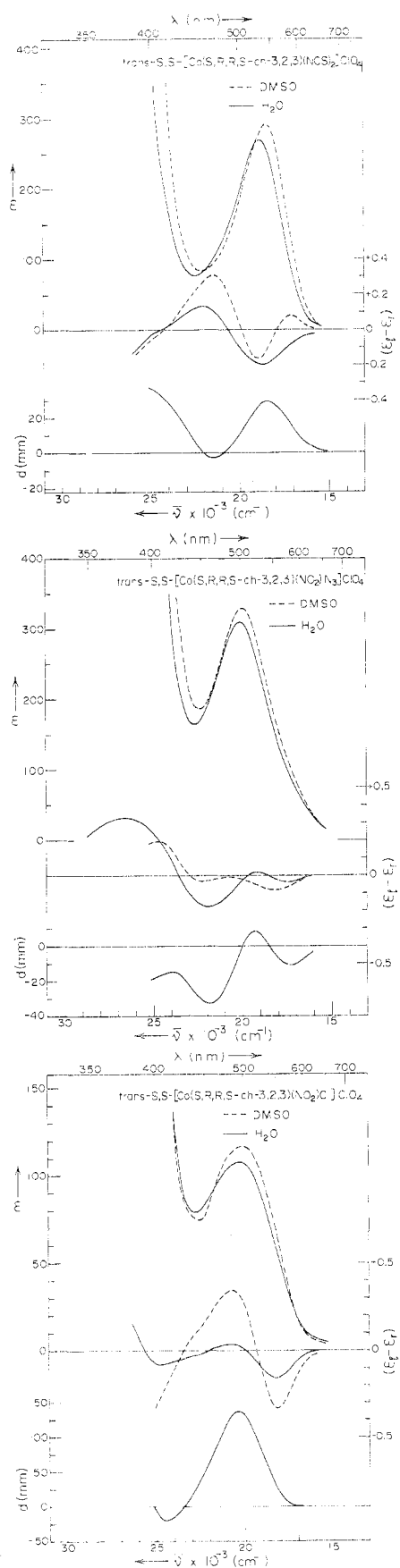


Figure 4.

dichroism emanating contiguously from the ${}^1T_{1g}$ and ${}^1T_{2g}$ manifolds. If this is so, then the ${}^1T_{1g}$ manifold has three resolved circular dichroism components at 19,000, 21,000, and

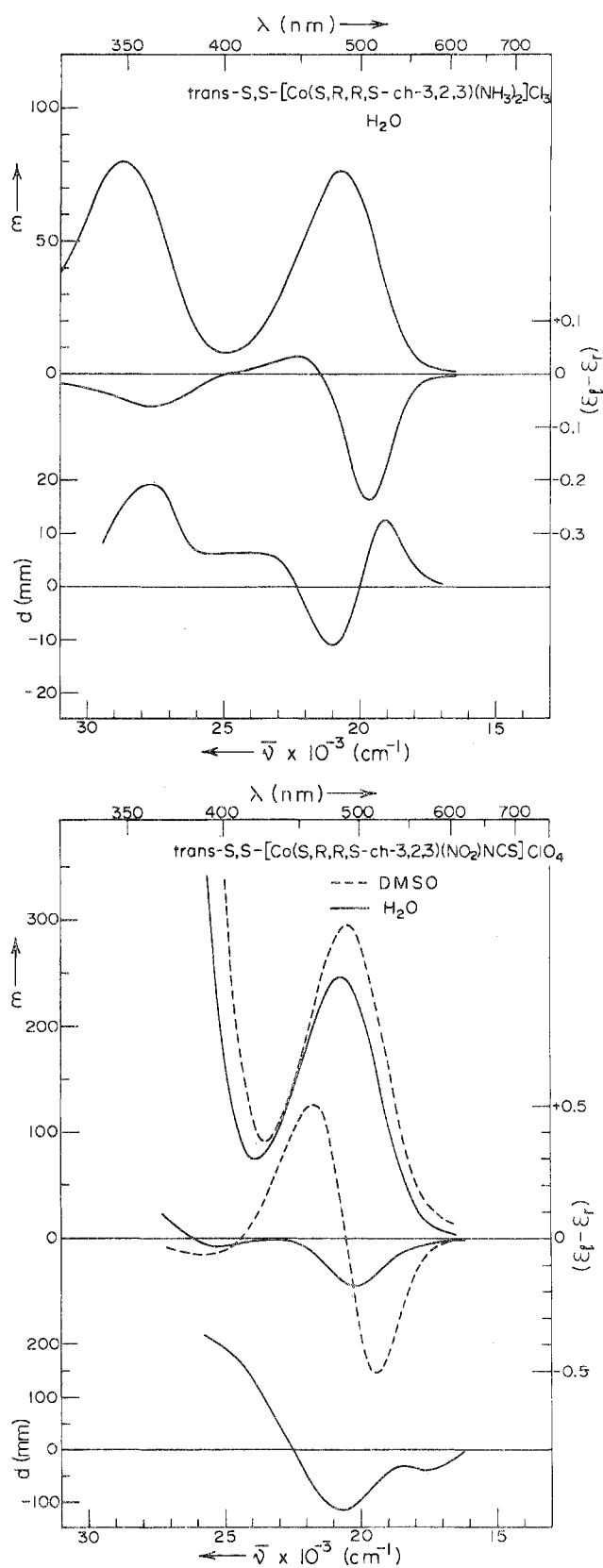


Figure 5.

23,500 cm^{-1} . This, to our knowledge, has not been observed before for chiral hexaammines and suggests that the 1E_g band, presumably lying to lower energies, is split into a couplet. This, however, does not appear to be the case in solution, where the 1E_g band, as in the case of the 3,2,3-tet analog, gives a dominant negative component, although the unsubstituted

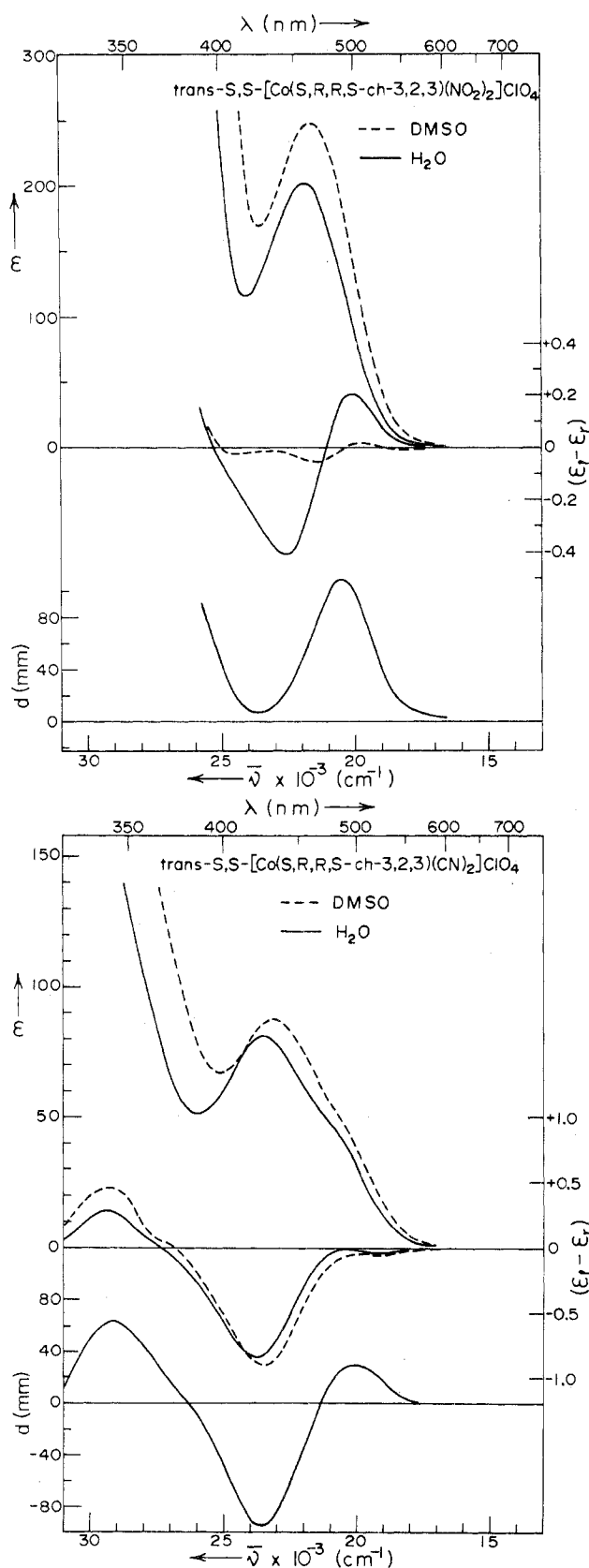


Figure 6.

analog does not reveal a ${}^1A_{2g}$ band in either the solution or solid-state spectra.

5. Complexes with Strong Axial Fields

The two complexes $trans\text{-}S,S\text{-}[\text{Co}(S,R,R,S\text{-}ch\text{-}3,2,3)\text{-}(\text{NO}_2)_2]\text{ClO}_4$ and $trans\text{-}S,S\text{-}[\text{Co}(S,R,R,S\text{-}ch\text{-}3,2,3)\text{-}$

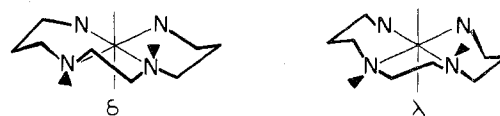


Figure 7. Two $trans$ conformations of a 3,2,3-tet type amine where, within the same chirality of the inner nitrogen atoms, the inner ring flips from δ to λ . With the given absolute configuration of the inner nitrogen atoms, the structure on the left is much more stable than the other.

$(\text{CN})_2]\text{ClO}_4$ have strong axial fields so that the ${}^1A_{2g}$ band lies to lower energies compared to the 1E_g band. Their spectra are shown in Figure 6, where it will be seen that the dicyano complex shows circular dichroism patterns in all corresponding cases, which are essentially the same as in the 3,2,3-tet complex.

The circular dichroism of the dinitro perchlorate salt in the solid state is similar to that of the bromide salt of the 3,2,3-tet analog but is different from that of the latter as the perchlorate salt. The aqueous solution spectra of the two series are similar but the present system in DMSO shows, by comparison with the aqueous solution spectrum, almost negligible circular dichroism under the ${}^1T_{1g}$ manifold. In addition, the ${}^1A_{2g}$ band appears to carry two very weak components.

6. Discussion

Before we discuss the implications of these results in relation to conformational instability, we briefly discuss the rather curious features observed in some of the very weak circular dichroism spectra. In the present series of complexes, the conformations are fixed and presumably contribute a constant amount of dissymmetric perturbation to the d electrons in all media, but the possibly opposing contributions from donor atom dissymmetry and dissymmetric solvation could vary from one medium to another. Thus we believe that when the circular dichroism spectra are almost "washed out," these opposing effects are nearly in balance.

The observation that when the spectra are very weakly dichroic, some complexes carry more components than there are spin-allowed transitions in the particular manifold suggests either of two explanations: either these extra bands are associated with spin-forbidden transitions or there is more than one species in solution. It is difficult to disprove the first, but we are inclined to the second explanation where, as the compounds are pure and stable, it is assumed that different solvated complexes will coexist in rapid equilibrium with each other, but the time scale of an electronic transition is such that the resultant observed spectrum is the concentration-weighted sum of all the contributing species in solution. If it is the case that different species exist in solution, then, on the basis of the large solvent variations observed in these complexes, it is plausible to suppose that the circular dichroism spectrum of each of the species could be different with respect to intensity and sign for certain bands and, in addition, the bandwidths and the energy positions of the compounds may be slightly different. With these assumptions, it is not difficult to envisage superimposed sets of spectra which could plausibly give rise to the effects observed.

In Table I the analogous circular dichroism data of the two series of complexes are collected; the sign of the particular spectroscopic component of the ${}^1T_{1g}$ manifold is indicated. Although some of the assignments are open to question, particularly when the levels are closely spaced, this does not vitiate the general conclusions we wish to draw from the results. For the present series, only spectra in DMSO and either in water or methanol are reported. Where possible, we have also run the spectra in DMF and, as for the unsubstituted systems, some variations occur, but the greatest changes occur in transferring from dipolar protic to dipolar aprotic solvents. Thus for simplicity, and since the essential point seems to

Table I

<i>trans-R,R</i> -[Co(3,2,3-tet)XY]Z					<i>trans-S,S</i> -[Co(<i>S,R,R,S</i> -ch-3,2,3)XY]Z				
XY	Z	Medium	¹ A _{2g}	¹ E _g λ →	XY	Z	Medium	¹ A _{2g}	¹ E _g λ →
Cl ₂	Cl ⁻	CH ₃ OH	--	+--	Cl ₂	Cl ⁻	CH ₃ OH	+--	+--
		DMSO	--	--			DMSO	+--	--
(NO ₃) ₂	NO ₃ ⁻	Solid	+	--	(NO ₃) ₂	NO ₃ ⁻	Solid	+	--
		CH ₃ OH	--	--			CH ₃ OH	+	--
(N ₃) ₂	ClO ₄ ⁻	Solid	--	+--	(N ₃) ₂	ClO ₄ ⁻	Solid	+	--
		H ₂ O	--	+--			H ₂ O	--	+--
(NCS) ₂	ClO ₄ ⁻	DMSO	+	--	(NCS) ₂	ClO ₄ ⁻	DMSO	+	--
		Solid	--	+--			Solid	--	+--
(NO ₂)N ₃	ClO ₄ ⁻	H ₂ O	--	--	(NO ₂)N ₃	ClO ₄ ⁻	H ₂ O	--	--
		DMSO	+	--			DMSO	+	--
(NO ₂)Cl	ClO ₄ ⁻	Solid	+	--	(NO ₂)Cl	ClO ₄ ⁻	Solid	--	+--
		DMF	+	--			CH ₃ OH	+	--
(NO ₂)NCS	ClO ₄ ⁻	Solid	+ (?)	(?)	(NO ₂)NCS	ClO ₄ ⁻	Solid	+ (?)	(?)
		H ₂ O	-- (?)	(?)			H ₂ O	-- (?)	(?)
(NH ₃) ₂	3Cl ⁻	DMF	+	--	(NH ₃) ₂	3Cl ⁻	DMF	+	--
		Solid	+	--			Solid	--	--
(NO ₂) ₂	ClO ₄ ⁻	H ₂ O	(?)	--	(NO ₂) ₂	ClO ₄ ⁻	H ₂ O	+	--
		Solid	(?)	--			Solid	+	--
(CN) ₂	ClO ₄ ⁻	H ₂ O	+	--	(CN) ₂	ClO ₄ ⁻	H ₂ O	+	--
		DMSO	+	--			DMSO	+--	(?)
	ClO ₄ ⁻	Solid	+	--		ClO ₄ ⁻	Solid	+	--
		H ₂ O	--	--			H ₂ O	--	--
		DMSO	--	--			DMSO	--	--
		Solid	+	--			Solid	+	--

emerge without these additional solvent data, we have included one example of each class of solvent in the table.

Two conclusions can be drawn from the data shown and tabulated here and shown in the previous paper. First, both systems show variations in transferring from one medium to another which are of the same order of magnitude. Second, although there is a partial correlation between the circular dichroism shown by analogous complexes of the two series in a given environment, there are a significant number of exceptions. However, the fact that the systems with fixed (chair) terminal rings show as much variation as the 3,2,3-tet analogs suggests that in neither series are conformational changes in the terminal rings responsible for the effects observed. Because these medium effects are so gross, we were concerned about ascribing them to solvent or crystal packing interactions. One other possible source of conformational instability considered was the central five-membered ring which, for a given absolute configuration of the inner nitrogen atoms, could conceivably flip from δ to λ or *vice versa* (Figure 7). If this were to happen to varying extents in various media then, since this ring is the major source of dissymmetry, the effects observed could be rationalized.

This possibility is almost certainly not an ambiguity in these systems. Conformational strain energy calculations by Busch³ show that the energy difference between the conformational isomers derived from flipping the inner ring is so large that, for a given chirality of the inner nitrogen atoms, the chirality of the inner ring is uniquely specified. In particular, the complexes, *trans-R,R*-[M(3,2,3-tet)XY]ⁿ⁺ and *trans-S,S*-[M(*S,R,R,S*-ch-3,2,3)XY]ⁿ⁺ will have δ rings (Figure 1); the λ ring in these complexes is of much higher energy because of the ring strain caused by forcing the terminal ring carbon atoms attached to the inner nitrogen atoms to adopt quasiallial dispositions (Figure 7). These predictions are confirmed by experiment³ and by the two crystal structures of the 3,2,3-tet-Co^{III} complexes.^{4,5} We therefore conclude that the

variations observed in the circular dichroism spectra in both the substituted and unsubstituted systems are not due to conformational changes but are medium effects.

On the basis of the results given here and in the previous papers, this conclusion would perhaps not be totally convincing because of some of the disparities between the substituted and unsubstituted systems. The conclusion, however, becomes realistically inescapable when the circular dichroism spectra of the analogous compounds with locked skew terminal chelate rings are considered. This is the subject of the next two papers.

7. Experimental Section

The preparations and resolutions of the various compounds are described in the preceding paper,² as is the instrumentation. As before, we have taken care to ensure that the recorded spectra are what they are claimed to be and that no solvolysis or substitution reactions occurred during the time of measurement.

Acknowledgment. We thank the Chemistry Department and the National Research Council of Canada for financial support.

Registry No. *trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)Cl₂]ClO₄, 53860-86-9; *trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)Cl₂]Cl, 53834-23-4; *trans-R,S*-[Co(*S,R,R,S*-ch-3,2,3)Cl₂]ClO₄, 53834-30-3; *trans-S,S*-[Co(*R,S,R,S*-ch-3,2,3)Cl₂]ClO₄, 53834-42-7; *trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)(N₃)₂]ClO₄, 36464-25-2; *trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)(NO₃)₂]NO₃, 53783-42-9; *trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)(NCS)₂]ClO₄, 53860-91-6; *trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)(NO₂)N₃]ClO₄, 53834-37-0; *trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)(NO₂)Cl]ClO₄, 53834-39-2; *trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)(NH₃)₂]Cl₃, 53834-35-8; *trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)(NCS)]ClO₄, 53860-93-8; *trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)(NO₂)₂]ClO₄, 53860-84-7; *trans-S,S*-[Co(*S,R,R,S*-ch-3,2,3)(CN)₂]ClO₄, 53834-34-7.

References and Notes

- (1) B. Bosnich and J. MacB. Harrowfield, *Inorg. Chem.*, **14**, 828 (1975).
- (2) B. Bosnich and J. MacB. Harrowfield, *Inorg. Chem.*, **14**, 836 (1975).
- (3) L. J. DeHayes and D. H. Busch, *Inorg. Chem.*, **12**, 2010 (1973).
- (4) N. C. Payne, *Inorg. Chem.*, **11**, 1376 (1972).
- (5) N. C. Payne, *Inorg. Chem.*, **12**, 1151 (1973).