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Dissymmetric Arsine Complexes. Circular Dichroism Spectra of Linear Quadridentate Tetra(tertiary arsine) Complexes

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The chiral octahedral Λ-cis-α and Δ-cis-β complexes of cobalt(III) coordinated to a linear quadridentate tetra(tertiary arsine) ligand give exceedingly complex circular dichroism patterns for their d–d electronic transitions. The origins of this complexity are discussed in terms of electronic and stereochemical effects. It is concluded that chiral complexes incorporating a majority of soft donor atoms give circular dichroism patterns that cannot be used easily to establish absolute configurations.

In the preceding paper the circular dichroism spectra of a series of *cis*-$[Co(diars)_2X_2]^{n+}$ complexes containing four soft donor arsenic atoms were presented and compared with analogous ethylenediamine compounds.[1] It was found that the d–d circular dichroism spectra were extremely sensitive to substitution of the (achiral) X groups. We now turn to a presentation and discussion of the data obtained for complexes of cobalt(III) containing a linear quadridentate tetra(tertiary arsine) ligand. This arsine ligand is structurally analogous to the previously studied linear tetra(tertiary amine) ligands, the cobalt(III) complexes of which give consistent patterns for the circular dichroisms associated with their d–d electronic transitions.[2-4] In view of the difficulties that arise in the interpretation of the circular dichroism data of linear quadridentate ligand complexes containing two sulfur atoms,[5] it is of some significance to establish the patterns observed for linear quadridentate systems containing a preponderance of soft donor atoms. It is for this reason that we chose to study the cobalt(III) complexes of *S*,*S*-tetars.

Stereochemistry and Spectroscopy

The structure of *S*,*S*-tetars is shown in Figure 1. Upon coordination, the chiral inner arsenic atoms induce complete stereospecificity in the topological chirality of the complexes.[6] That is, *R*,*R*-tetars (coordinated)[7] induces exclusively the Λ-*cis*-α-$[Co(R,R\text{-tetars})X_2]^{n+}$ and Δ-*cis*-β-$[Co(R,R\text{-tetars})X_2]^{n+}$ topological chiralities (Figure 1). In addition to the topological chirality, both the inner arsenic chirality and the chirality of the chelate-ring conformations can contribute to the circular dichroism of the complexes. Crystal structures of three tetars cobalt(III) complexes show that the terminal six-membered chelate rings exist in distorted chair conformations while the inner five-membered ring exists in the chiral gauche form.

The previous paper[1] outlined in detail the peculiarities of the d–d absorptions of [tetra(tertiary arsine)]cobalt(III) complexes and other spectroscopic considerations necessary for analyzing the circular dichroism data. We therefore will not repeat these here, but we refer to the previously determined relationship between the circular dichroism observed for the Λ-cis-α and Δ-cis-β absolute topologies of $[Co(trien)X_2]^{n+}$ complexes (trien = triethylenetetraamine). It was found[3] that the circular dichroism associated with the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition was opposite in sense for the Λ-cis-α and Δ-cis-β isomers, or more precisely the "major" $^1T_{1g}$ component reversed sign for the two absolute topologies. This relationship holds for similar linear tetraaminecobalt(III) complexes.[4,8] It was therefore of interest to determine whether this relationship held for the more complicated but analogous arsine complexes.

Results

We begin by discussing the Λ-cis-α- and Δ-cis-β-$[Co(R,R\text{-tetars})X_2]^{n+}$ complexes in which the X groups have a weaker crystal field than the arsenic donor atoms. In these cases the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition component, $^1A_1 \rightarrow {}^1B_1$, will occur at lower energies than the $^1A_1 \rightarrow {}^1A_2$, $^1B_2$ quasi-degenerate transition component.[1] The latter in (amine)cobalt(III) complexes usually gives the larger circular dichroism and has been used as an index of absolute configuration.[9] As we showed in the previous paper,[1] however, the $^1A_1 \rightarrow {}^1A_2$, $^1B_2$ transitions can give a plus–minus couplet for the circular dichroism, and hence in these cases the usefulness of these transitions for absolute configuration assignments is ambiguous.

The spectra of the Λ-cis-α and Δ-cis-β sulfato complexes are shown in Figures 2 and 3. In both of these complexes the sulfato ligand acts as a bidentate chelate.[10] The intense absorption band at around 30 000 cm^{-1} represents the arsenic to cobalt charge-transfer bands. Depending of the crystal field strength of the X groups, these bands will move in energy appropriately, but they occur at around this energy for all of the complexes although, in many cases, they are overlapped by cobalt-X charge-transfer bands and by the $^1A_{1g} \rightarrow {}^1T_{2g}$ transition. The two d–d bands, which occur at lower energies, are unusually intense and overlap one another.[1]

For the sulfato complexes, the $^1A_{1g} \rightarrow {}^1T_{2g}$ transition occurs at ~23 000 cm^{-1} and the magnetic dipole allowed $^1A_{1g} \rightarrow {}^1T_{1g}$ excitation appears at ~19 000 cm^{-1}. The circular dichroism associated with this latter transition is mainly positive for the Λ-cis-α complex and negative for the Δ-cis-β isomer. This, superficially, is the same pattern as is observed for the corresponding isomers of the $[Co(trien)X_2]^+$ series.[3] This consistency, however, may be an illusion.

The major positive band of the Λ-*cis*-α-$[Co(trien)X_2]^{n+}$ complexes is assumed to represent the $^1A_1 \rightarrow {}^1A_2$, $^1B_2$ component of the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition. This component should

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(1) Jackson, W. G.; McLaren, J. W.; Bosnich, B. *Inorg. Chem.*, companion paper in this issue.

(2) Hawkins, C. F. "Absolute Configuration of Metal Complexes"; Cotton, F. A., Wilkinson, G., Eds.; Wiley-Interscience: New York, 1971.

(3) Sargeson, A. M.; Searle, G. H. *Inorg. Chem.* **1965**, *4*, 45.

(4) Bosnich, B.; Harrowfield, J. M.; Boucher, H. *Inorg. Chem.* **1975**, *14*, 815.

(5) Bosnich, B.; Phillip, A. T. *J. Chem. Soc. A* **1970**, 264.

(6) Bosnich, B.; Jackson, W. G.; Wild, S. B. *J. Am. Chem. Soc.* **1973**, *95*, 8269.

(7) Upon coordination to cobalt(III), free *S*,*S*-tetars is designated *R*,*R*-tetars (coordinated) according to the accepted priority rules. There is no change in absolute configuration (see ref 6).

(8) Cragel, J.; Brubaker, G. R. *Inorg. Chem.* **1972**, *11*, 303.

(9) McCaffery, A. J.; Mason, S. F.; Norman, B. J. *J. Chem. Soc.* **1965**, 5094.

(10) Bosnich, B.; Jackson, W. G.; Wild, S. B. *Inorg. Chem.* **1974**, *13*, 1121. Bosnich, B.; Jackson, W. G.; Lo, S. T. D.; McLaren, J. W. *Ibid.* **1974**, *13*, 2605.

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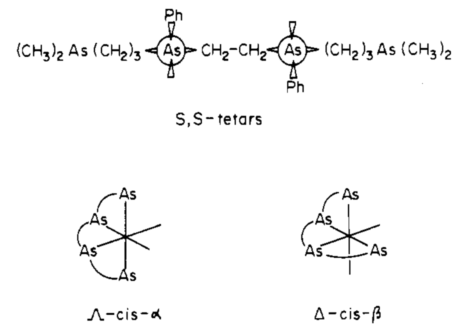

Figure 1. Structures of *S*,*S*-tetars and the Λ-*cis*-α- and Δ-*cis*-β-$[Co(R,R\text{-tetars})X_2]^{n+}$ isomers.

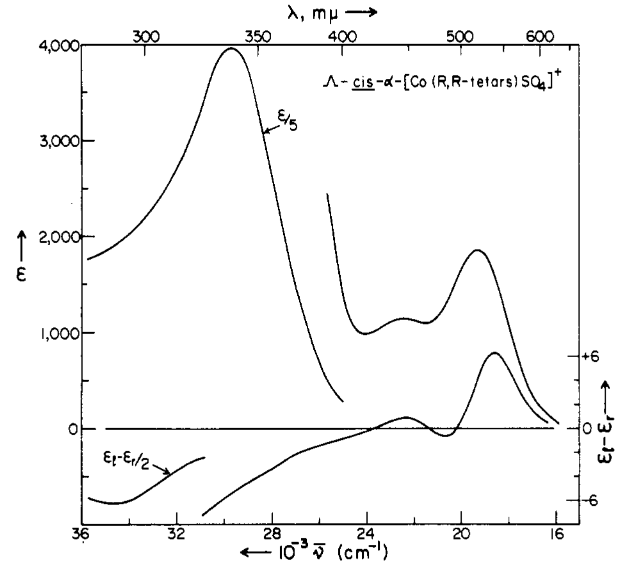

Figure 2. Absorption and circular dichroism spectra of Λ-*cis*-α-$[Co(R,R\text{-tetars})SO_4]ClO_4$ in acetonitrile solution.

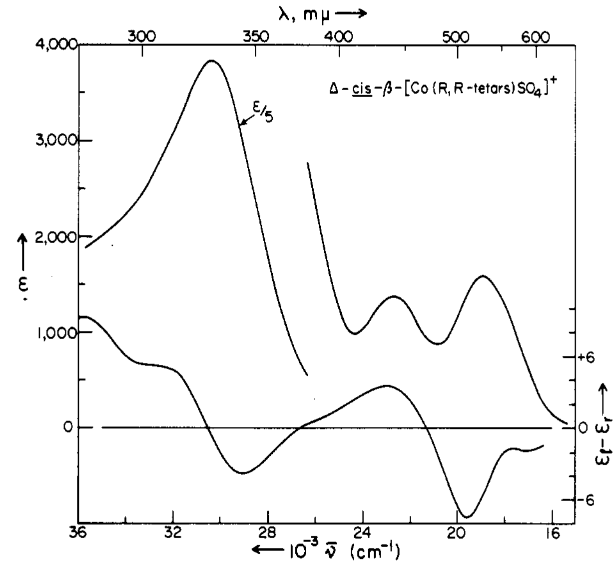

Figure 3. Absorption and circular dichroism spectra of Δ-*cis*-β-$[Co(R,R\text{-tetars})SO_4]ClO_4$ in acetonitrile solution.

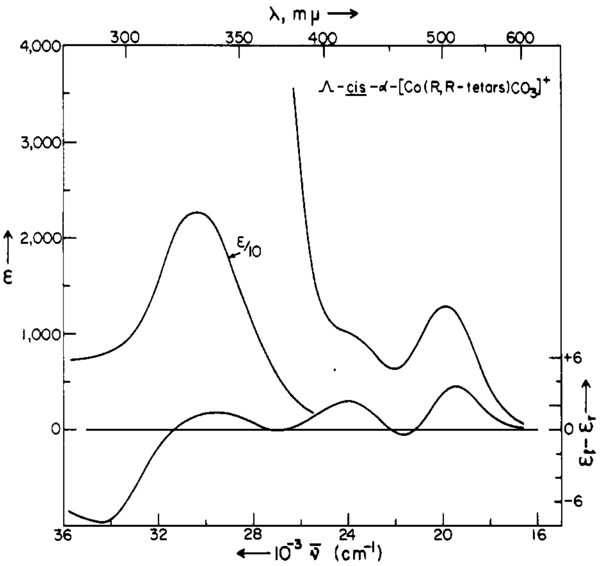

Figure 4. Absorption and circular dichroism spectra of Λ-*cis*-α-$[Co(R,R\text{-tetars})CO_3]ClO_4$ in methanol solution.

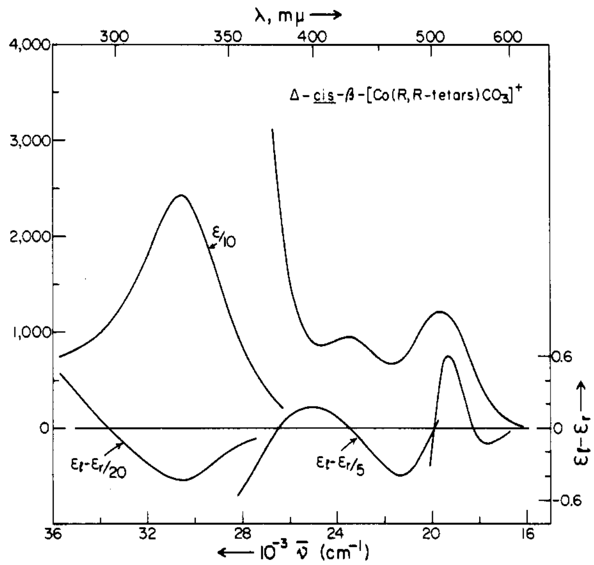

Figure 5. Absorption and circular dichroism spectra of Δ-*cis*-β-$[Co(R,R\text{-tetars})CO_3]ClO_4$ in methanol solution.

occur to the higher energy side of the $^1T_{1g}$ manifold for sulfato complexes. The lower energy component $^1A_1 \rightarrow {}^1B_1$ carries negative circular dichroism for some of the Λ-*cis*-α-$[Co(trien)X_2]^{n+}$ species. Therefore with the normal splitting pattern assumed,[11] the strong positive circular dichroism component at ~18 500 cm^{-1} seen for Λ-*cis*-α-$[Co(R,R\text{-tetars})SO_4]^+$ may represent the $^1A_1 \rightarrow {}^1B_1$ transition and the $^1A_1 \rightarrow {}^1A_2$, $^1B_2$ component may carry the weaker circular dichroism at ~20 500 cm^{-1}. If this is so, then the pattern observed for the circular dichroism of this arsine complex is opposite to that observed for the trien analogues.

An alternative explanation is that the resultant $^1T_{1g}$ circular dichroism is dominated by the $^1A_1 \rightarrow {}^1A_2$, $^1B_2$ components, which are split into a plus-minus couplet as is observed for some of the *cis*-$[Co(diars)_2X_2]^+$ species, and the $^1A_1 \rightarrow {}^1B_1$ circular dichroism is not resolved because of overlap with the strong positive band. Such an explanation, of course, makes any connection between circular dichroism and absolute structure even more difficult to ascertain.

For the Δ-*cis*-β sulfato complex both circular dichroism components, $^1A_1 \rightarrow {}^1B_1$ (~17 000 cm^{-1}) and $^1A_1 \rightarrow {}^1A_2$, $^1B_2$ (~19 500 cm^{-1}), are negative, and by the major band criterion, this is consistent with spectra observed for the trien complexes. However, the negative minimum at ~17 750 cm^{-1} may indicate the presence of a positive component.

The carbonato complexes (Figures 4 and 5) have similar structural and electronic characteristics as the analogous sulfato isomers. The appearance of a major positive $^1T_{1g}$ circular dichroism band for the Λ-cis-α carbonato isomer is

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[11] Yamatera, H. *Bull. Chem. Soc. Jpn.* **1958**, *31*, 95.

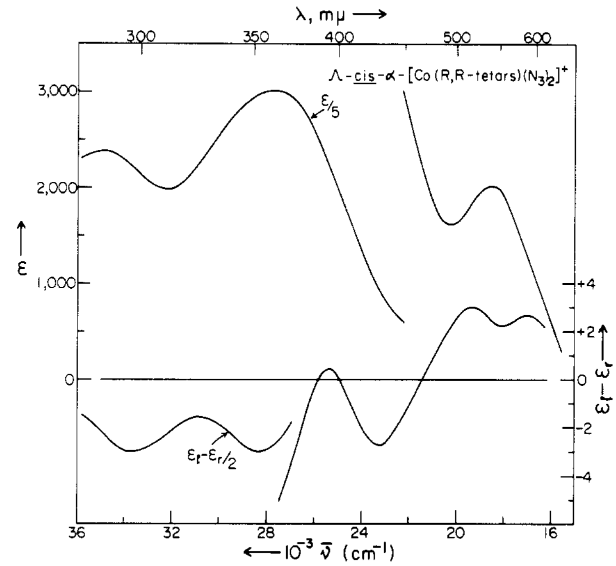

Figure 6. Absorption and circular dichroism spectra of Λ-*cis*-α-[Co(*R*,*R*-tetars)$(N_3)_2$]ClO_4 in methanol solution.

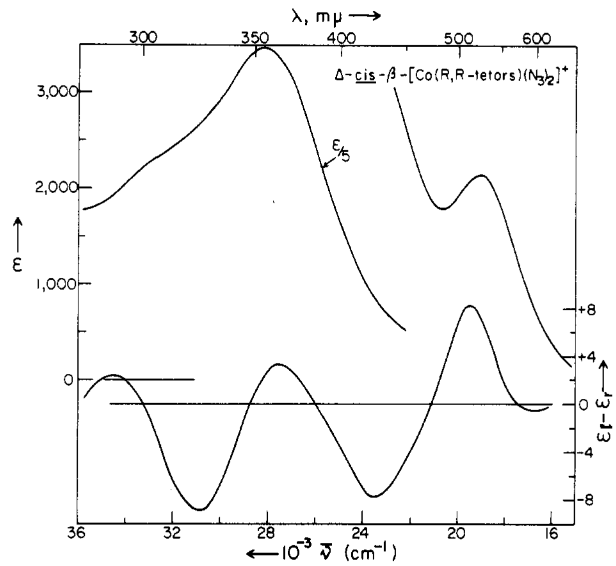

Figure 7. Absorption and circular dichroism spectra of Δ-*cis*-β-[Co(*R*,*R*-tetars)$(N_3)_2$]ClO_4 in methanol solution.

superficially similar to the case of the spectrum observed for the trien analogue except that, in this arsine case, a weaker negative band is present to higher energies (~21 500 cm^{-1}). We therefore assume that the couplet arises from the $^1A_1 \rightarrow {}^1A_2$, $^1B_2$ transitions. That a couplet can be observed for these components is seen for the circular dichroism of the Δ-cis-β carbonato species where the three $^1T_{1g}$ components occur as a (−),(+),(−) triplet of absorptions. It is clear that the "major band" criterion cannot be applied to this isomer.

The cis diazido complexes, Figures 6 and 7, show $^1T_{1g}$ circular dichroism that reveals two positive bands for the Λ-cis-α isomer whereas the Δ-cis-β diazido isomer shows, contrary to the analogous trien isomer, a major positive band and a weak negative band to lower energies. The Λ-cis-α diazido isomer has a positive minimum at ~18 000 cm^{-1}, which may indicate the presence of a negative component which is not observed as such because of the two strong contiguous positive components.

The diisothiocyanato isomers, Figures 8 and 9, have $^1T_{1g}$ circular dichroism, which consists of a single positive band for the Λ-cis-α complex and of a (+),(−),(+) triplet of absorptions for the Δ-cis-β species. It will be noted that the Δ-cis-β carbonato isomer also shows a triplet but in the *reverse sense.*

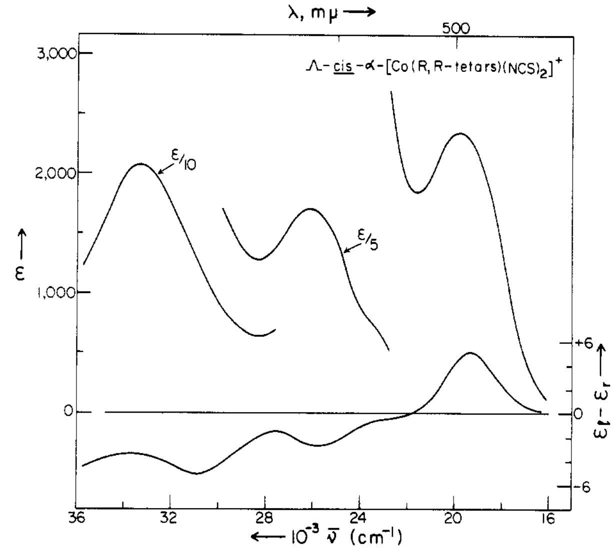

Figure 8. Absorption and circular dichroism spectra of Λ-*cis*-α-[Co(*R*,*R*-tetars)$(NCS)_2$]ClO_4 in methanol solution.

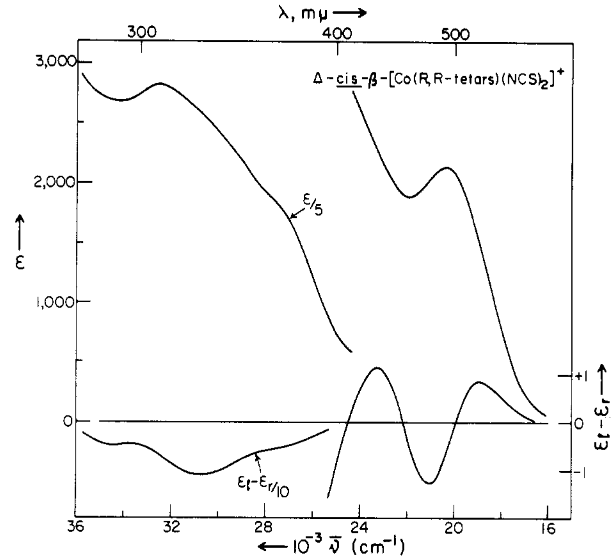

Figure 9. Absorption and circular dichroism spectra of Δ-*cis*-β-[Co(*R*,*R*-tetars)$(NCS)_2$]ClO_4 in methanol solution.

We have no explanation for this remarkable reversal.

The crystal field strength of the nitro ligand is only slightly weaker than that of the arsenic donor atoms.[1] As a result, we expect the components of the $^1T_{1g}$ manifold to be closely spaced in energy, and hence the net sign of the $^1T_{1g}$ circular dichroism is expected to reflect the sign of the most intense component. Despite this, the $^1T_{1g}$ circular dichroism of the Λ-cis-α dinitro isomer (Figure 10) consists of a (+),(−) couplet of roughly equal intensity, and that of the Δ-cis-β dinitro complex (Figure 11) is also seen as a couplet except that the positive component is dominant. Thus, compared to the trien analogues, the Λ-cis-α isomer does not provide an obvious index of absolute configuration, and the Δ-cis-β isomer gives the opposite sign pattern to that observed for the trien analogue.

Finally, we show in Figure 12 the absorption and circular dichroism spectra of the Λ-*cis*-α-[Co(*R*,*R*-tetars)$(CN)_2$]$^+$ ion. The dicyano complexes are formed under equilibrium conditions mediated by Co(II) electron transfer, and we were unable to detect the Δ-cis-β isomer, only the cis-α and trans isomers were detected under these conditions. The CN^- ligand has a higher crystal field than the tertiary arsine donors, and hence, the $^1T_{1g}$ splitting pattern for this complex should be reversed compared to those of all of the other complexes

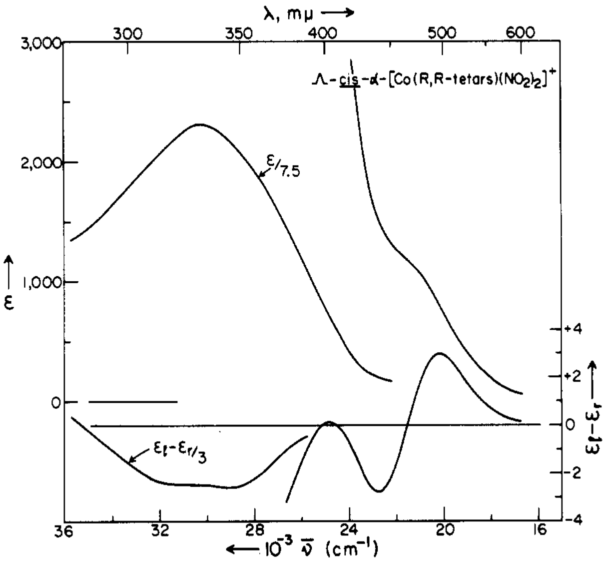

Figure 10. Absorption and circular dichroism spectra of Λ-*cis*-α-[Co(*R*,*R*-tetars)$(NO_2)_2]ClO_4$ in methanol solution.

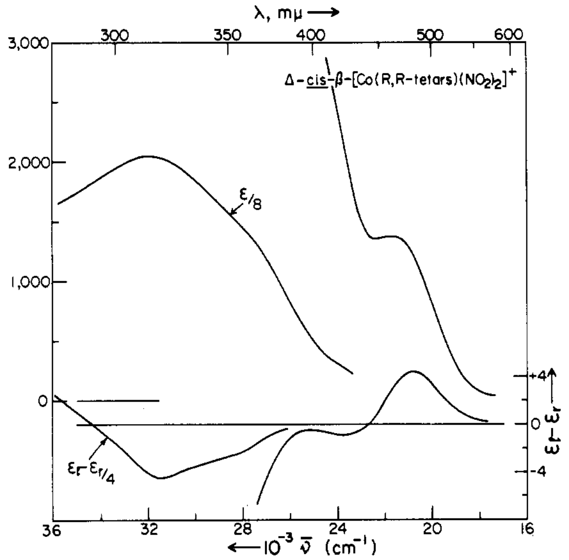

Figure 11. Absorption and circular dichroism spectra of Δ-*cis*-β-[Co(*R*,*R*-tetars)$(NO_2)_2]ClO_4$ in acetonitrile solution.

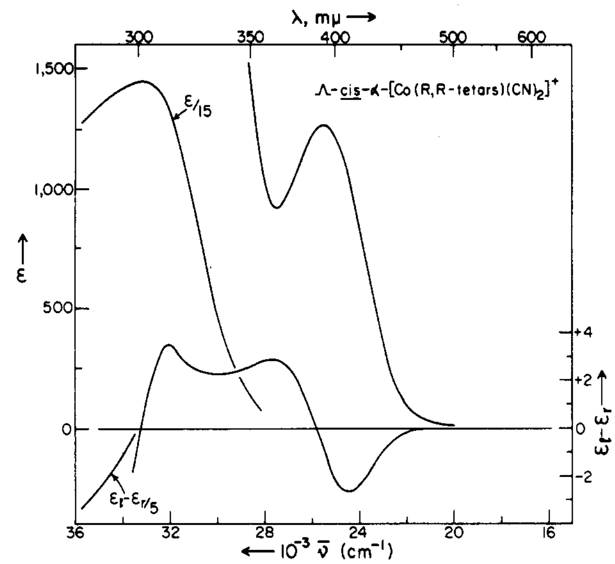

Figure 12. Absorption and circular dichroism spectra of Λ-*cis*-α-[Co(*R*,*R*-tetars)$(CN)_2]ClO_4$ in methanol solution.

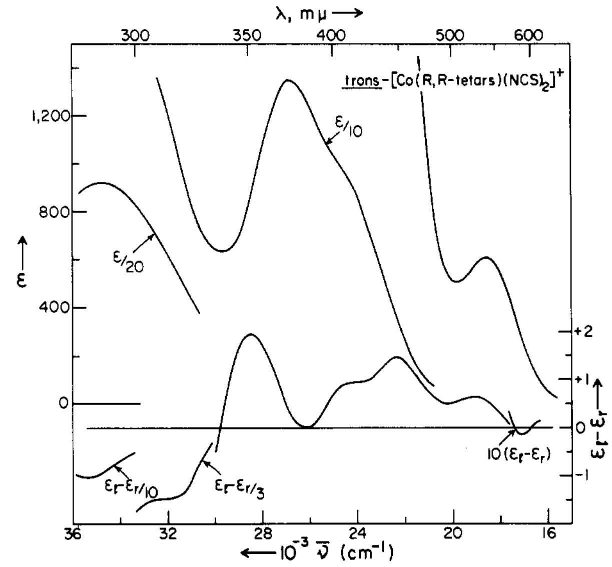

Figure 13. Absorption and circular dichroism spectra of *trans*-[Co(*R*,*R*-tetars)$(NCS)_2]ClO_4$ in methanol solution.

discussed here. That is, the $^1A_1 \rightarrow {}^1B_1$ component should be of higher energy compared to the $^1A_1 \rightarrow {}^1A_2$, $^1B_2$ components for the dicyano species, whereas the reverse holds true for the other cis complexes discussed here. In view of this, the $^1T_{1g}$ circular dichroism pattern of the Λ-cis-α dicyano complex is the same as that observed for the Λ-cis-α dinitro species if it is assumed that the same components are involved for both cases. Like the dinitro analogue, the Λ-cis-α dicyano species' $^1T_{1g}$ circular dichroism has no obvious major band.

Discussion

The preceding results serve to illustrate the sensitivity of the circular dichroism spectra of cobalt(III) arsine complexes to apparently trivial substitutions of the X groups. This sensitivity has not been observed before for hard donor atom systems. In particular the $^1T_{1g}$ circular dichroism of cobalt(III) linear quadridentate amine complexes is remarkably consistent, despite the variety of ligand structural types that have been studied.[2] It is therefore difficult to accede to the supposition that the inconsistencies found for the present complexes are predominantly connected with the chiral complexities of the coordinated tetars structure although they may be an important consideration.

Such a supposition would invoke the interplay of contributions due to the topological chirality, the chirality of the inner arsenic atoms, and the conformational chirality of the chelate rings, which may vary as X or the topology is varied. It is not inconceivable that circular dichroism due to these last two effects could be comparable to that due to the topological chirality. That this may be so is supported by the spectra of the *trans*-[Co(*R*,*R*-tetars)$X_2]^+$ complexes (X = NCS^-, NO_2^-, CN^-) shown in Figures 13–15. It will be seen that the $^1T_{1g}$ circular dichroism of the trans dinitro and trans dicyano complexes are as intense as that observed for the corresponding cis complexes and that the trans diisothiocyanato complex shows the (+),(−),(+) triplet pattern observed in some of the cis complexes. Thus, the nontopological chiral induction can have an important influence on the resultant circular dichroism of the cis complexes. When we compare a series of homologous complexes, however, we are concerned not with the absolute magnitude of these nontopological effects but rather with the possible variation in these effects when the X groups and the topology are changed. Since the effect of the inner arsenic chirality is expected to remain roughly constant, any

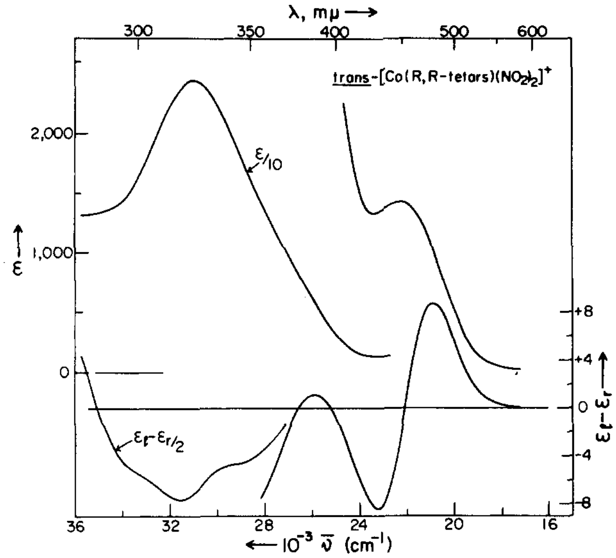

Figure 14. Absorption and circular dichroism spectra of *trans*-[Co(*R*,*R*-tetars)(NO$_2$)$_2$]ClO$_4$ in methanol solution.

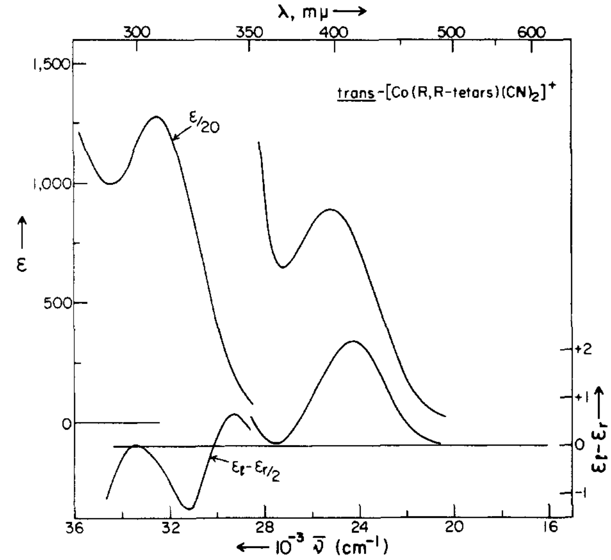

Figure 15. Absorption and circular dichroism spectra of *trans*-[Co(*R*,*R*-tetars)(CN)$_2$]ClO$_4$ in methanol solution.

variations in chiral induction would be mainly connected with chelate-ring conformational changes. Within a topological series, the achiral X groups are unlikely to cause conformational changes although a cis-α to cis-β change may cause conformational adjustments. For the present series, however, we have observed inconsistencies not only between topologies but within a topological series. We therefore need to seek an electronic explanation.

The origins of these electronic effects may lie in the appearance of new charge-transfer circular dichroism bands that occur when the X groups are varied. Because there is undoubtedly strong mixing between these states and the d–d transitions,[1] the circular dichroism associated with these latter transitions could be strongly affected by the former. This effect can be qualitatively described, but it is difficult to quantify.

Although many of the variations observed for this series of complexes might be explained in qualitative terms by invoking stereochemical and electronic effects, the problem of the circular dichroism of the sulfato and carbonato complexes remains. These complexes are expected to have very similar electronic and structural characteristics, and yet the $^1T_{1g}$ circular dichroism they display is, at least superficially, very different. We have no persuasive explanation for these results.

Ideally, for empirical absolute configuration assignments, we require a single magnetic dipole allowed electronic transition that is well separated in energy from other transitions of the system. Such a situation does not exist for the d–d transitions of metal complexes where the $^1T_{1g}$ components are closely spaced in energy and each can carry its own sign so that the resultant circular dichroism can display a diversity of patterns depending on the mix of signs, intensities, and energy positions of the three components.[1] The results recorded for these arsine complexes illustrate how acute the problem can be.

Experimental Section

All of the complexes were prepared by methods described elsewhere.[10] Circular dichroism spectra were measured with a Roussell–Jouan Dichrographe II using a Xe lamp, and the linear absorptions were recorded on a Unicam SP 820 spectrophotometer.

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Registry No. Λ-*cis*-α-[Co(*R*,*R*-tetars)SO$_4$]ClO$_4$, 52225-15-7; Δ-*cis*-β-[Co(*R*,*R*-tetars)SO$_4$]ClO$_4$, 52225-17-9; Λ-*cis*-α-[Co(*R*,*R*-tetars)CO$_3$]ClO$_4$, 50804-63-2; Δ-*cis*-β-[Co(*R*,*R*-tetars)CO$_3$]ClO$_4$, 50804-57-4; Λ-*cis*-α-[Co(*R*,*R*-tetars)(N$_3$)$_2$]ClO$_4$, 50804-47-2; Δ-*cis*-β-[Co(*R*,*R*-tetars)(N$_3$)$_2$]ClO$_4$, 50804-49-4; Λ-*cis*-α-[Co(*R*,*R*-tetars)(NCS)$_2$]ClO$_4$, 50804-23-4; Δ-*cis*-β-[Co(*R*,*R*-tetars)(NCS)$_2$]ClO$_4$, 50804-25-6; Λ-*cis*-α-[Co(*R*,*R*-tetars)(NO$_2$)$_2$]ClO$_4$, 50804-35-8; Δ-*cis*-β-[Co(*R*,*R*-tetars)(NO$_2$)$_2$]ClO$_4$, 50804-37-0; Λ-*cis*-α-[Co(*R*,*R*-tetars)(CN)$_2$]ClO$_4$, 50804-13-2; *trans*-[Co(*R*,*R*-tetars)(NCS)$_2$]ClO$_4$, 50804-27-8; *trans*-[Co(*R*,*R*-tetars)(NO$_2$)$_2$]ClO$_4$, 50804-39-2; *trans*-[Co(*R*,*R*-tetars)(CN)$_2$]ClO$_4$, 50804-15-4.