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Dissymmetric Arsine Complexes. An Analysis of the Circular Dichroism Spectra of Chiral Diarsine Complexes of Cobalt(III)

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The circular dichroism spectra of a series of *cis*-di-X-bis[*o*-phenylenebis(dimethylarsine)]cobalt(III) complexes (*cis*-$[Co(diars)_2X_2]^{n+}$) are described. Their absolute configurations are inferred from exciton theory. The circular dichroism associated with the d–d electronic transitions shows complex patterns. This complexity is ascribed to the sensitivity of these transitions to mixing with higher energy states of the system that occurs to a greater extent when soft rather than hard ligands coordinate to the metal.

The correlations of the absolute configurations of transition-metal complexes with the circular dichroism associated with their d–d transitions have been the subject of numerous investigations.[1] Despite this considerable effort, very few general correlations have been supported by subsequent experiments. It does appear, however, that the simple bis-bidentate and tris-bidentate configurationally dissymmetric complexes of cobalt(III) and chromium(III) show acceptably consistent circular dichroism for their magnetic dipole allowed d–d transitions. Similarly, the exciton coupling theory[2] involving quasi-localized transitions associated with dissymmetrically disposed conjugated ligands seems generally reliable, despite the somewhat severe approximations used in the simple weak-coupling theory.

Nearly all of the work done on configurationally dissymmetric complexes has involved systems containing the hard donor atoms oxygen and nitrogen. Such systems respond fairly well to the classic crystal field analysis,[3] but it remains to be seen whether soft donor atom systems, such as arsenic, phosphorus, and perhaps sulfur,[4] are susceptible to such treatment. It is known[5] that the usual zero-order selection rules are considerably relaxed in such systems, leading to extensive mixing of the electronic states partly as a result of the diminution of the interelectronic repulsion parameters.[6]

In this and the following paper, we present data for cobalt(III) complexes containing four arsenic donor atoms. This paper describes spectra of the simplest possible systems: configurationally dissymmetric bis-bidentate tertiary arsine complexes that are devoid of the complexities of conformational dissymmetry. The following paper deals with more complicated systems involving a quadridentate tetra(tertiary arsine) ligand that forms octahedral complexes having conformational as well as configurational dissymmetry.

Stereochemical and Spectroscopic Considerations

The systems discussed are the *cis*-bis[*o*-phenylenebis(dimethylarsine)]di-X-cobalt(III) complexes, *cis*-$[Co(diars)_2X_2]^{n+}$. The structure of the ligand is shown in Figure 1. All of the complexes discussed refer to the same absolute configuration, which, as we shall show, is the one (Λ) shown in Figures 4–9.

In order to illustrate the pronounced changes that occur in the d–d spectra of cobalt(III) complexes when soft donor atoms replace hard donor ligands, we show the d–d spectra of the two ions *cis*-$[Co(en)_2CO_3]^+$ and *cis*-$[Co(diars)_2CO_3]^+$ in Figure 2 (en = ethylenediamine). There are two striking differences shown by these spectra. First, the extinction coefficients of the spectra for the diarsine complex are 5 times larger ($\epsilon \sim 1000$) than those corresponding to the amine complex. The second difference relates to the separation between the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ (lower energy) and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ (higher energy) manifold of transitions of the two complexes. Whereas the *cis*-$[Co(en)_2CO_3]^+$ complex shows a separation of $\sim$8000 cm^{-1}, the *cis*-$[Co(diars)_2CO_3]^+$ species has a corresponding separation of only $\sim$4000 cm^{-1} for the ${}^1T_{1g}$ and ${}^1T_{2g}$ manifolds. The relative intensities of the two complexes suggest that for the arsine complex the d states are more strongly mixed with other higher energy states of the system, making the crystal field approximation less reliable than for the amine system. A smaller separation between the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transitions is another manifestation of greater mixing and directly reflects a reduction in the interelectronic repulsions between states because of the greater diffuseness of the d functions in the arsine complex.

Because the states are so strongly mixed in the arsine complex, the zero-order selection rules are unlikely to survive in the lower symmetry arsine complexes. Thus the classical argument[3] that, because the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ excitation is magnetic dipole allowed and the ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transition is magnetic dipole forbidden, the former should carry much stronger circular dichroism is likely to break down. This could lead to both of the spin-allowed transitions having comparable circular dichroism. Under these conditions it is not clear how the signs and magnitudes of the circular dichroism bands under the hitherto diagnostic ${}^1T_{1g}$ manifold will distribute themselves. This and the following paper explore these problems experimentally.

Absolute Configurations

The relative absolute configurations of the chiral *cis*-$[Co(diars)_2X_2]^{n+}$ complexes have been established by chemical interconversions.[6] The absolute configurations of a number of the key derivatives can be determined from the exciton circular dichroism of the dissymmetrically disposed diars ligands.[2]

The $\pi \rightarrow \pi^*$ transitions of the benzene ring of the diars ligand are polarized in the molecular plane and are directed either along the twofold rotation axis (z) or perpendicular to it (x) (Figure 1). When two diars ligands form a chiral cis-bis-bidentate octahedral complex, the localized $\pi \rightarrow \pi^*$ transitions interact and combine to give exciton coupling modes. The z-axis-polarized transitions couple only to produce electric transition dipole moments and do not generate the necessary zero-order collinear magnetic transition dipole moments for optical activity. Both of the coupling modes generated by the x-axis-polarized excitations, however, give rise to orthogonally polarized components, each having collinear electric and magnetic transition dipole moments. These

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(1) Hawkins, C. F. "Absolute Configuration of Metal Complexes"; Cotton, F. A., Wilkinson, G., Eds.; Wiley-Interscience: New York, 1971.
(2) Bosnich, B. *Acc. Chem. Res.* **1969**, *2*, 266.
(3) Moffit, W. *J. Chem. Phys.* **1956**, *25*, 1189.
(4) Bosnich, B.; Phillip, A. T. *J. Chem. Soc. A* **1970**, 264.
(5) (a) Dunn, T. M.; Nyholm, R. S.; Yamada, S. *J. Chem. Soc.* **1962**, 1564. (b) Feltham, R. D.; Silverthorn, W. *Inorg. Chem.* **1968**, *7*, 1154. (c) Bosnich, B.; Jackson, W. G.; Wild, S. B. *J. Am. Chem. Soc.* **1973**, *95*, 8269.
(6) Bosnich, B.; Jackson, W. G.; McLaren, J. W. *Inorg. Chem.* **1974**, *13*, 1133.

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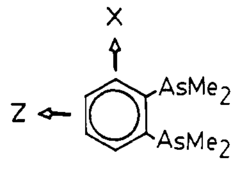

Figure 1. Structure of the ligand diars.

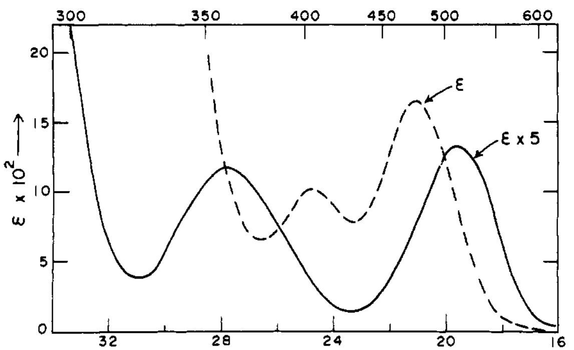

Figure 2. Absorption spectra of *cis*-$[Co(en)_2CO_3]^+$ in water (—) and of *cis*-$[Co(diars)_2CO_3]^+$ in methanol (- - -) solutions.

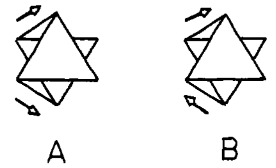

Figure 3. Two exciton coupling modes involving the *x*-axis-polarized transitions of the benzene ring of diars.

latter modes are shown in Figure 3; mode A gives positive circular dichroism whereas mode B gives equal negative circular dichroism for the absolute configuration shown. The usual exciton splitting pattern[7] will therefore give a positive (lower energy)–negative (higher energy) circular dichroism couplet under the *x*-axis-polarized transitions of diars for the Λ absolute configuration.

The allowed *x*-axis-polarized $\pi \rightarrow \pi^*$ transition of catechol occurs at around 51 000 cm^{-1},[8] and we assume that it will also occur in this region for diars. Our instrument did not allow us to go above ~54 000 cm^{-1}, and so we were unable to obtain the full exciton spectrum. It will be seen, however, that, for the three complexes drawn, whose spectra are shown in Figures 4–6, the circular dichroism spectrum at ~51 000 cm^{-1} is positive and exceedingly intense. Moreover, in each case the positive band is contiguous with a negative band at higher energies.

The optically active tris(catecholato)arsenic(V) anion[8] also has a strong circular dichroism couplet in this region and has a similar normalized[2] intensity. It seems reasonable, therefore, to assign the intense positive circular dichroism band at ~ 51 000 cm^{-1} to the lower energy component of an exciton couplet so that the absolute configuration of these complexes is Λ as shown. The absolute configurations of the other complexes described here follow from the chemical interconversions.[6]

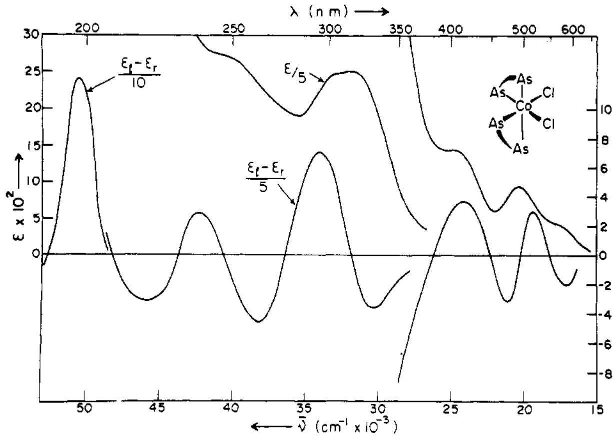

Figure 4. Absorption and circular dichroism spectra of Λ-*cis*-$[Co(diars)_2Cl_2]ClO_4$ in methanol solution.

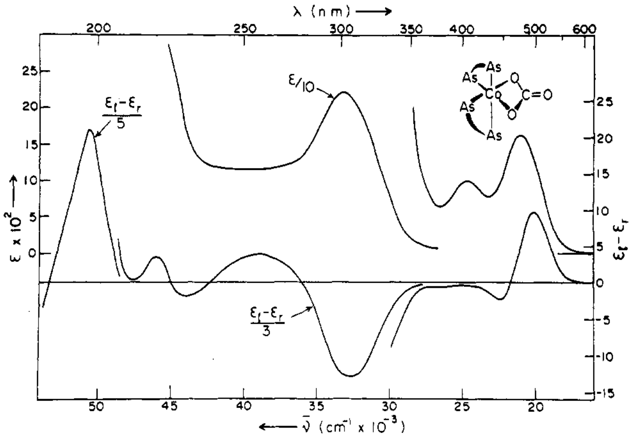

Figure 5. Absorption and circular dichroism spectra of Λ-*cis*-$[Co(diars)_2CO_3]ClO_4$ in methanol solution.

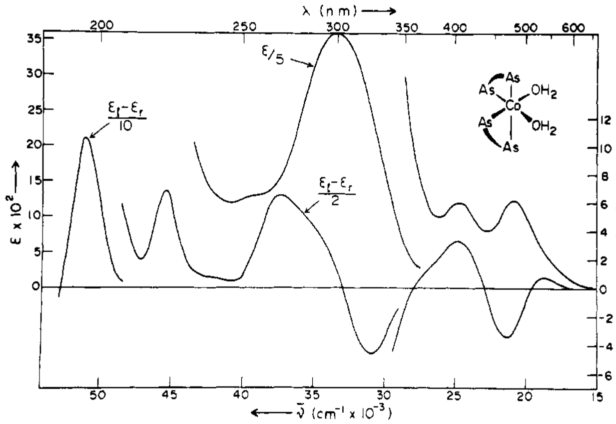

Figure 6. Absorption and circular dichroism spectra of Λ-*cis*-$[Co(diars)_2(H_2O)_2]^{3+}$ in 1.0 M $HClO_4$-water solution.

Spectroscopic Assignments

In order to discuss the circular dichroism spectra associated with the d–d transitions with precision, each component transition must be assigned and only equivalent spectroscopic transitions should be compared. We consider mainly the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition because, unlike its $^1A_{1g} \rightarrow {}^1T_{2g}$ counterpart, it is magnetic dipole allowed, it is usually not obscured by other transitions, and it is the transition that has been used for absolute configuration determinations.

In the C_2 field of the complexes discussed here, the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition is split, and although the linear absorption may not reveal this splitting, the circular differential absorption usually does. An approximate estimate of the splitting of the $^1T_{1g}$ manifold can be obtained from semiempirical molecular orbital theory.[9] Thus for the *cis*-$[Co(As)_4X_2]^{n+}$ chromophore,

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(7) Bosnich, B. *Inorg. Chem.* **1968**, *7*, 178.

(8) Ito, T.; Hanazaki, I.; Kobayashi, A.; Marumo, F.; Saito, Y. *Proc. Int. Conf. Coord. Chem. 14th* **1972**. Platt, J. R. *J. Chem. Phys.* **1951**, *19*, 263.

(9) Yamatera, H. *Bull. Chem. Soc. Jpn.* **1958**, *31*, 95.

the $^1A_{1g} \rightarrow {}^1T_{1g}$ excitation in O_h will split under the C_{2v} field as follows: $^1A_1 \rightarrow {}^1B_1$, $E + {}^1/_2\delta$; $^1A_1 \rightarrow {}^1A_2$, $^1B_2$, $E + {}^1/_4\delta$. In this approximation the $^1A_2$ and $^1B_2$ upper levels are degenerate, and we have combined σ- and π-bonding in one parameter δ. Thus E is the energy of the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition of the $[Co(As)_6]^{3+}$ chromophore, and δ is the difference in energy between the $^1A_{1g} \rightarrow {}^1T_{1g}$ transitions of the $[Co(As)_6]^{3+}$ and $[Co(X)_6]^{n+}$ chromophores.

The $^1A_{1g} \rightarrow {}^1T_{1g}$ band of the $[Co(diars)_3]^{3+}$ complex occurs at 23 200 cm^{-1},[5b] and hence all of the X groups, except the NO_2^- ligand, in the *cis*-$[Co(diars)_2X_2]^{n+}$ species discussed here will have a weaker crystal field than the $[Co(As)_6]^{3+}$ chromophore. It follows, therefore, that the $^1A_1 \rightarrow {}^1B_1$ component of the $^1T_{1g}$ manifold will occur at lower energies compared to the $^1A_1 \rightarrow {}^1A_2$, $^1B_2$ transitions for these complexes.

For *cis*-$[Co(en)_2X_2]^{n+}$ complexes having the Λ absolute configurations,[10,11] two types of circular dichroism patterns are observed under the $^1T_{1g}$ manifold. When the X ligands have either a much weaker (e.g., Cl^-) or a much stronger (e.g., NO_2^-) crystal field compared to that of ethylenediamine, the $^1A_1 \rightarrow {}^1B_1$ transition is negative and the $^1A_1 \rightarrow {}^1A_2$, $^1B_2$ transitions are positive and the latter carries the stronger circular dichroism. When the ligands X and ethylenediamine have similar crystal fields (e.g., $X_2 = CO_3^-$), the stronger $^1A_1 \rightarrow {}^1A_2$, $^1B_2$ circular dichroism band dominates and generally only a positive band is observed under the $^1T_{1g}$ manifold. There are variations in the above pattern among other configurationally dissymmetric cobalt(III) complexes containing hard donor atom ligands,[1] but it is generally possible to assign the absolute configurations on the basis of the sign of the major circular dichroism component under the $^1T_{1g}$ manifold.

Circular Dichroism Spectra

Figure 4 shows the absorption and circular dichroism spectra of the Λ-*cis*-$[Co(diars)_2Cl_2]^+$ ion. The $^1T_{1g}$ manifold shows splitting in the linear absorption with peaks at ~17 000 and 21 000 cm^{-1}. The $^1A_{1g} \rightarrow {}^1T_{2g}$ transition occurs as a shoulder at ~25 000 cm^{-1} and is overlapped by two charge-transfer bands that are centered at ~34 000 cm^{-1}. These latter transitions probably involve excitations of the σ electrons of the chloro and arsenic ligands to antibonding levels derived from the metal d orbitals and the ligand σ orbitals. In all of the other complexes described here, an intense absorption at ~34 000 cm^{-1} is observed, and because no such band occurs in these regions for the corresponding ethylenediamine complexes, it seems plausible to ascribe it to an arsenic to cobalt charge-transfer band. Transitions to higher energies (>34 000 cm^{-1}) involve, among others, transitions localized on the benzene rings and will not concern us further.

The lowest energy d–d circular dichroism absorption, $^1A_1 \rightarrow {}^1B_1$ of $^1A_{1g} \rightarrow {}^1T_{1g}$ parentage, occurs at ~17 000 cm^{-1} and is negative as is the same transition for Λ-*cis*-$[Co(en)_2Cl_2]^+$. Unlike the case of Λ-*cis*-$[Co(en)_2Cl_2]^+$, however, where the $^1A_1 \rightarrow {}^1A_2$, $^1B_2$ components of $^1A_{1g} \rightarrow {}^1T_{1g}$ appear as a single positive band, the diarsine analogue gives a positive (~19 000 cm^{-1}) and negative (~21 000 cm^{-1}) couplet for these two components. That the zero-order selection rules[3] do not necessarily apply for arsine complexes is shown by the similar circular dichroism intensities observed under both the $^1T_{1g}$ and $^1T_{2g}$ manifolds; a relatively strong positive band at ~24 000 cm^{-1} is observed under the latter.

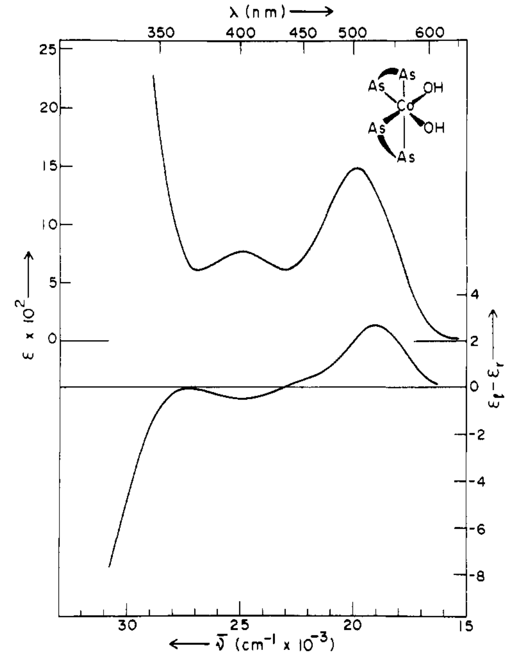

Figure 7. Absorption and circular dichroism spectra of Λ-*cis*-$[Co(diars)_2(OH)_2]^+$ in 0.1 N NaOH–water solution.

This last observation is not necessarily characteristic of arsine complexes because it will be seen that the circular dichroism is relatively weak under the $^1T_{2g}$ manifold for Λ-*cis*-$[Co(diars)_2CO_3]^+$ (Figure 5). The $^1A_{1g} \rightarrow {}^1T_{1g}$ transition of the carbonato complex is quite different from that of the dichloro analogue, the former only carrying positive (~20 000 cm^{-1}) and weaker negative (~23 000 cm^{-1}) circular dichroism components.

Although the Λ-*cis*-$[Co(diars)_2(H_2O)_2]^{3+}$ (Figure 6) and Λ-*cis*-$[Co(diars)_2(OH)_2]^+$ (Figure 7) ions have two oxygen donor atoms like the carbonato analogue and hence presumably have similar electronic characteristics, the diaquo and dihydroxo species show different circular dichroism behavior. The circular dichroism under the $^1T_{2g}$ manifold of the diaquo complex is strongly positive (~25 000 cm^{-1}) relative to the corresponding components under the $^1T_{1g}$ band whereas, like the carbonato analogue, the dihydroxo species shows relatively weak negative circular dichroism under the $^1T_{2g}$ band (~25 000 cm^{-1}). The $^1T_{1g}$ components also show different patterns for the diaquo and the dihydroxo complexes, and each of these is different from the carbonato analogue; the dihydroxo species shows only a single positive component (~24 000 cm^{-1}) whereas the diaquo complex gives a couplet (~19 000 and 21 000 cm^{-1}).

It could be argued that the overall charges of the carbonato, diaquo, and dihydroxo complexes may be connected with the similarity of the circular dichroism spectra of the unipositively charged species. This supposition cannot be sustained, however, because the Λ-*cis*-$[Co(diars)_2(NO_3)_2]^+$ complex displays a circular dichroism spectrum (Figure 8) similar to that of the diaquo complex under both the $^1T_{1g}$ and $^1T_{2g}$ manifolds.

The d–d spectra of Λ-*cis*-$[Co(diars)_2(NO_2)_2]^+$ (Figure 9) are overlapped by higher energy charge-transfer bands, and the $^1T_{1g}$ absorption (~23 000 cm^{-1}) shows a relatively weak circular dichroism couplet (~20 000 and ~23 000 cm^{-1}). The NO_2^- and arsine ligands have very similar crystal fields, and it is not possible to assign the components with certainty. Because the splitting of the $^1T_{1g}$ manifold is small, there will be extensive overlap of the circular dichroism bands and this may explain the relative weakness of the circular differential absorption. The sign pattern is similar to that observed for the carbonato, diaquo, and dinitrato complexes.

Discussion

It is clear that the present series of complexes do not display circular dichroism patterns associated with their $^1T_{1g}$ manifolds, which could be used to assign their absolute configu-

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(10) Reference 1, pp 218–220.

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

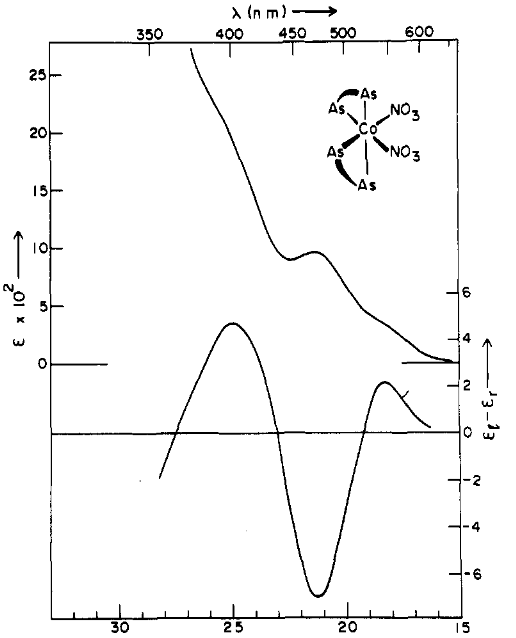

Figure 8. Absorption and circular dichroism spectra of Λ-*cis*-$[Co(diars)_2(NO_3)_2]ClO_4$ in methanol solution.

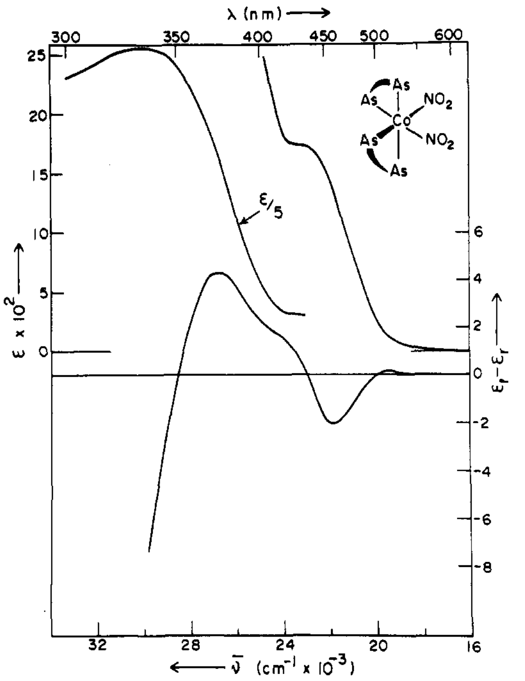

Figure 9. Absorption and circular dichroism spectra of Λ-*cis*-$[Co(diars)_2(NO_2)_2]ClO_4$ in methanol solution.

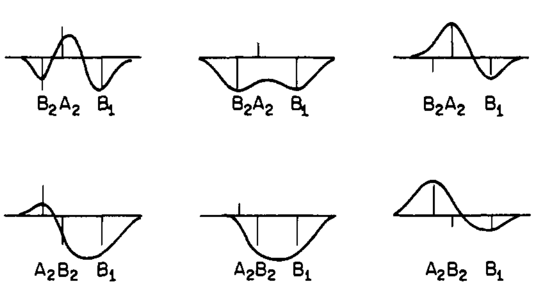

Figure 10. Possible ${}^1T_{1g}$ circular dichroism patterns for a Λ-*cis*-$[Co(bidentate)_2X_2]^{n+}$ complex, where the crystal field of X is less than that of the donor atoms of the bidentate. The outcome does not depend on assuming that the A_2 component is positive and the B_2 component is negative; these have been chosen arbitrarily. Energy increases to the left.

rations in a simple and general way. The question as to whether the soft diarsine ligand systems are in a fundamental sense different from the hard ligand systems seems worth pursuing. Because of the low-lying charge-transfer states and the sharp decrease in the interelectronic repulsions, the d levels have lost much more of their free-ion character in the soft ligand complexes than in the classical hard donor atom compounds. Thus through more extensive mixing, the spectral characteristics of the d–d transitions are more sensitive to the new charge-transfer bands appearing upon substitution in soft ligand systems. Since the circular dichroism associated with the d–d transitions is to a greater or lesser extent borrowed from the charge-transfer states, these too will be more sensitive to substitution in soft ligand complexes. This may explain the sharp variations in circular dichroism intensities and sign patterns observed upon apparently trivial substitution in the present series of complexes.

It is, however, possible to argue, with modest conviction, that essentially the same ${}^1T_{1g}$ circular dichroism patterns obtain for both the *cis*-$[Co(diars)_2X_2]^{n+}$ and *cis*-$[Co(en)_2X_2]^{n+}$ complexes and that the apparent disparities manifest themselves because of variations in intensity and energy position of the three closely spaced levels.

Suppose it is assumed that all Λ-*cis*-$[Co(bidentate)_2X_2]^{n+}$ complexes, irrespective of the hardness or softness of the ligands, will have the same sign pattern as is observed for the three ${}^1T_{1g}$ components of the Λ-*cis*-$[Co(diars)_2Cl_2]^+$ ion. The ${}^1A_1 \rightarrow {}^1B_1$ transition occurs at the lowest energy and is negative for both the Λ-*cis*-$[Co(diars)_2Cl_2]^+$ and Λ-*cis*-$[Co(en)_2Cl_2]^+$ ions. Semiempirical molecular orbital theory[9] does not separate the ${}^1A_1 \rightarrow {}^1A_2$, ${}^1B_2$ transitions in energy; subtle effects could cause the levels to split, and the sense of the splitting is not easily predicted. In Figure 10, we show six possible circular dichroism patterns that could be observed by simply varying the relative intensities of the components and interchanging the ordering of the A_2 and B_2 levels. It is not difficult to imagine additional resultant patterns, but the diagrams in Figure 10 serve to illustrate how it is possible to get all of the experimentally observed ${}^1T_{1g}$ circular dichroism patterns without assuming that any one of the components changes sign for the same absolute configuration.

Such an explanation, if correct, is less than satisfactory for engendering confidence in assignment of absolute configurations. The apparent consistencies in the circular dichroism patterns for hard ligand systems is probably connected with the lower degree of variation of mixing of the d levels with other states of the system compared to soft donor atom complexes. Our present complexes, which have four soft arsenic donor atoms, may serve to illustrate how borrowing can give a variety of resultant circular dichroism patterns for the same absolute configuration when three closely spaced levels are involved, even if each of the components retains the same sign from complex to complex.

Experimental Section

The complexes were prepared and the absolute configurations were correlated by methods reported previously.[6] Circular dichroism spectra were measured with a Roussell-Jouan Dichrographe II using a Xe lamp, and the linear absorptions were recorded on a Unicam SP820 spectrophotometer.

Acknowledgment. This work was supported by grants from the Natural Sciences and Engineering Research Council of Canada.

Registry No. Λ-*cis*-$[Co(diars)_2Cl_2]ClO_4$, 51051-01-5; Λ-*cis*-$[Co(diars)_2CO_3]ClO_4$, 51018-03-2; Λ-*cis*-$[Co(diars)_2(H_2O)_2]^{3+}$, 51018-00-9; Λ-*cis*-$[Co(diars)_2(OH_2)]^+$, 86480-61-7; Λ-*cis*-$[Co(diars)_2(NO_3)_2]ClO_4$, 51063-05-9; Λ-*cis*-$[Co(diars)_2(NO_2)_2]ClO_4$, 50805-03-3; *cis*-$[Co(en)_2CO_3]^+$, 17835-73-3; *cis*-$[Co(diars)_2CO_3]^+$, 51017-97-1.