Conclusions

On the basis of these calculations for σ-bonding, weakly π-bonding, and strongly π-bonding situations for CN^-, we can draw the following conclusions. (1) One must exercise care in deducing a CN force constant change from a frequency shift. (2) On the basis of the correlation between F_{CN} and overlap energy, the LCAO-MO method used in these studies faithfully reproduces, at least within a related series, the changes in CN binding when CN^- coordinates a Lewis acid. (3) CN σ binding strengthens when either the carbon or nitrogen lone pair coordinates—though to a lesser extent with strongly back-bonding acids. (4) These computations provide no evidence for the operation of synergism in the coordination of CN^-, in the sense that the greater σ withdrawal by X the greater π donation by X. (4) The degree of back-bonding depends strongly on overlap integrals and energy matching of the π^*- and acid π-type orbitals. (6) Estimates of electric field gradients at the nitrogen atom in XCN by this MO method are better than for those at halogens; nevertheless, the errors associated with the MO method and the model for analysis of quadrupole data do not invalidate any of the trends in field gradient magnitude. (7) The computations reveal an increased basicity of the nitrogen lone pair when carbon coordination occurs, and there is experimental justification of this prediction.

Acknowledgment. The author wishes to thank the Bell Telephone Laboratories of Winston-Salem for their generous donation of IBM 7040/7044 computer time. He also wishes to express his appreciation to Jeanne Boone of Bell Laboratories for her assistance in performing these computations.

Asymmetric Syntheses, Asymmetric Transformations, and Asymmetric Inductions in an Optically Active Solvent

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Abstract: Asymmetric syntheses, asymmetric transformations, and asymmetric inductions have been achieved using L-2,3-butanediol as a solvent. When a solution of the racemic *cis*-dichlorobis(ethylenediamine)cobalt(III) ion is heated in the optically active solvent, the ion slowly antiracemizes to give an optically active product. Similar asymmetric syntheses occur with the *cis*-dichlorobis(ethylenediamine)chromium(III) ion and with the α-*cis*-dichlorotriethylenetetraminecobalt(III) ion; at equilibrium the latter complex exists as a mixture of α- and β-*cis* isomers both of which are optically active. In this solvent *trans*-chlorohydroxobis(ethylenediamine)cobalt(III) chloride isomerizes to the *cis* isomer which is optically active. In all these asymmetric syntheses resolution appears to be total. Dissolution of *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride in the active solvent results in the appearance of strong optical activity in the region of the d → d absorption of the ion. This is regarded as a first-order asymmetric transformation wherein the solvent constrains the puckered ethylenediamine–cobalt rings into one of their enantiomeric conformations. Benzil and benzophenone dissolved in L-2,3-butanediol show optical activity in the region of the n → π^* carbonyl absorption. These effects are regarded as examples of asymmetric induction which, presumably, is evident because of hydrogen bonding between the solvent and the carbonyl group.

The equilibrium constant between the enantiomeric forms of an optically active substance dissolved in an optically inactive medium is unity, and thus the sum of the contributions to the optical activity by the two enantiomorphs is zero. In certain cases, however, the addition of an optically active substance to such solutions leads to a displacement of the equilibrium and hence to the observation that the racemic mixture, in solution, has been either partly or totally resolved. This effect was named by Kuhn[1] as an "asymmetric transformation of the first order (or kind)." Similarly he named the earlier observation of Leuchs and Wutke,[2] who found that brucine precipitated *chemically* quantitative amounts of only one enantiomer of 2-*o*-carboxybenzyl-α-hydrindone from acetone solution, as an "asymmetric transformation of the second order." These two phenomena have been observed extensively in both organic[3] and inorganic[4] systems. In the latter compounds these effects have been variously described as "configurational activity"[5] or simply as the "Pfeiffer effect"[6] although Werner[7] observed essentially the same effect almost 20 years before. There seems little doubt that, in general terms, in both the first- and second-order asymmetric transformations, the basic physical mechanism which controls these effects is the same, namely, that an asymmetric molecule, whether in the crystal or in solution, interacts differently with the left- and right-handed forms of the molecules undergoing the asymmetric transformation.

The recognition of this fundamental principle, that asymmetry begets asymmetry, leads naturally to the supposition that asymmetric transformations, asymmetric syntheses, and asymmetric inductions may be observed in a suitable asymmetric solvent. Although

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[1] R. Kuhn, *Ber.*, **65**, 49 (1932).

[2] H. Leuchs and J. Wutke, *ibid.*, **46**, 2420 (1913).

[3] E. E. Turner and M. M. Harris, *Quart. Rev.* (London), **1**, 299 (1947).

[4] F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p 285.

[5] F. P. Dwyer, D. F. O'Dwyer, and E. C. Gyarfas, *Nature*, **167**, 1036 (1951).

[6] P. Pfeiffer and K. Quehl, *Ber.*, **64**, 2667 (1931).

[7] A. Werner, *ibid.*, **45**, 3061 (1912).

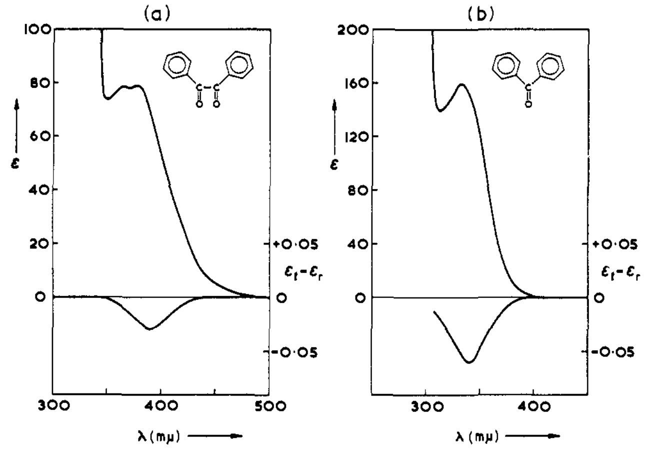

Figure 1. The absorption spectra of (a) benzil and (b) benzophenone and their associated circular dichroism in L-2,3-butanediol.

it is taken as axiomatic that an asymmetric molecule will "contemplate" differently left- and right-handed chemical species and physical environments, and also that a molecule devoid of the geometric prerequisites for optical activity will be asymmetrically perturbed by an asymmetric compound or physical environment, the actual observation of these effects is dependent upon the magnitude of the detailed energetics resulting from the asymmetric discrimination or perturbation. Many attempts have been made in order to observe these effects in asymmetric solvents[8] but, except for two reported examples,[8] the results have been either unsuccessful or inconclusive.

We wish here to report and describe examples of asymmetric syntheses, asymmetric transformations, and asymmetric inductions[8] using the optically active solvent L-2,3-butanediol.

Results

I. **Asymmetric Inductions**. The n → π* transition of the carbonyl chromophore involves the promotion of a nonbonding electron of the oxygen atom to the antibonding π orbital formed by the carbon and oxygen atoms of the group. Molecules possessing a plane of symmetry coincident with the carbonyl π-orbital plane make this transition magnetic dipole allowed but electric dipole forbidden. If such an excitation involved only the pure p-atomic functions, the transition would have a magnetic dipole transition moment of $\sqrt{2}\,\beta$ (β = Bohr magneton) polarized along the carbonyl bond axis. This value is considerably reduced when the p-orbital functions become involved in the formation of the carbonyl bond. In general, magnetic dipole transitions have low dipole strengths but, relative to the dipole strength in optically active molecules, the rotational strength is large. It is clear, therefore, that if asymmetric induction is to be observed it will be most easily evident in the absorption regions of magnetic dipole allowed transitions. This has already been confirmed by our recent observation[8] that the planar $[PtCl_4]^{2-}$ ion shows asymmetric induction in the region of one of the magnetic dipole d → d transitions. The two systems discussed here are benzil and benzophenone.

In both these systems the n → π* absorptions are enhanced in intensity and displaced to lower energies compared to formaldehyde. These two observations are consistent with the assumption that the carbonyl chromophore electrons interact with those mainly localized on the benzene rings. Under these circumstances the n → π* transition will borrow intensity from allowed transitions of the phenyl groups and in so doing will be repelled to lower energies.

When benzil and benzophenone are dissolved in L-2,3-butanediol, the respective n → π* transitions show a single negative circular dichroic absorption (Figure 1). Both have low rotational strengths. Were these electronic transitions five times as strong, our instrument, having a sensitivity of 1.5×10^{-4}, would not have detected this activity. The induced circular dichroism must arise because the potential exerted by the solvent on the carbon chromophores is, on the time average, dissymmetric. We are uncertain as to the precise mechanism by which this can come about, but suspect that hydrogen bonding between the carbonyl group's lone-pair electrons and the hydrogen atoms of the solvent's hydroxyl group would help to set up a network of hydrogen bonds connecting the solute and the hydrogen-bonded bulk solvent to produce a relatively stationary and tight asymmetric cage about the chromophore. There is, however, another way in which optical activity might occur. It is possible that both benzil and benzophenone are solvated into some preferred dissymmetric configuration, thus making them optically active. We were unable to detect any activity under the n → π* transition of fluorenone, a planar and rigid carbonyl compound, and so both mechanisms remain as possibilities. In this connection it is perhaps relevant to point out that bis-N-methylacridinium nitrate showed no circular dichroism when dissolved in the active solvent. If the solvent was capable of dissymmetrically solvating aromatic rings to any appreciable extent, we would expect to observe circular dichroism in the region of the long-axis-polarized transitions of the acridine nucleus.

II. **Asymmetric Transformations**. The green-colored complex ion *trans*-dichlorobis(ethylenediamine)cobalt(III), *trans*-$[Co(en)_2Cl_2]^+$, can exist in three isomeric forms; one of which is optically inactive and the other two mutually enantiomeric. The isomerism arises because of the puckered[9,10] cobalt–ethylenediamine rings which are dissymmetric and may be arbitrarily called *d* and *l*. It is clear, therefore, that the complex ion *trans*-$[Co(en)_2Cl_2]^+$ might exist with either *dd*, *ll*, or *dl* ring conformations. In the first two cases the complex belongs to the point group D_2 and is optically active, whereas in the last case the complex belongs to the C_{2h} point group and is therefore an optically inactive *meso* form. The rate of interconversion of the *d* and *l* conformations in solution is probably fairly rapid, but can be "frozen" by use of optically bidentate diamines such as (−)-propylenediamine, where the interactive demands of the system[9] require an equatorially disposed methyl group which in turn constrains the rings to one conformation. Under these circumstances, the *trans*-diacidobis(−)-propylenediamine

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[8] (a) B. Bosnich, *J. Am. Chem. Soc.*, **88**, 2606 (1966); (b) G. Buchanan and S. H. Graham, *J. Chem. Soc.*, 500 (1950); (c) J. Glazer, M. M. Harris, and E. E. Turner, *ibid.*, 1753 (1950).

[9] E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959).

[10] Y. Saito, K. Nakatsu, M. Shiro, and H. Kuroya, *Bull. Chem. Soc. Japan*, **30**, 795 (1957).

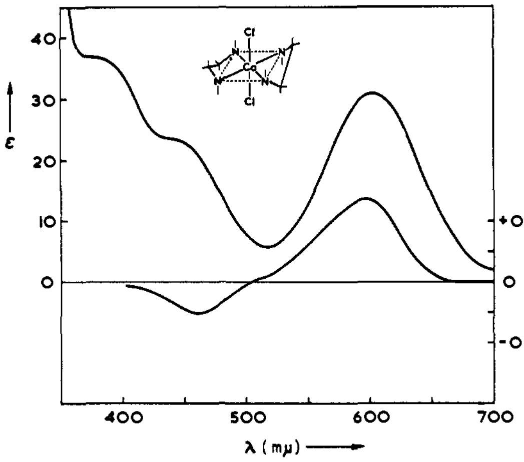

Figure 2. The visible absorption spectrum of *trans*-[Co(en)$_2$Cl$_2$]Cl and the associated circular dichroism in L-2,3-butanediol. The lack of symmetry of the positive circular dichroism peak at around 600 mμ is not significant, as the "sag" to lower energies is an instrumental characteristic and the hump to higher energies probably arises from the slight amount of resolved *cis* isomer that may be formed during the measurement of the spectrum. Shown also is the suggested absolute configuration of the ethylenediamine rings of *trans*-[Co(en)$_2$Cl$_2$]$^+$ in L-2,3-butanediol.

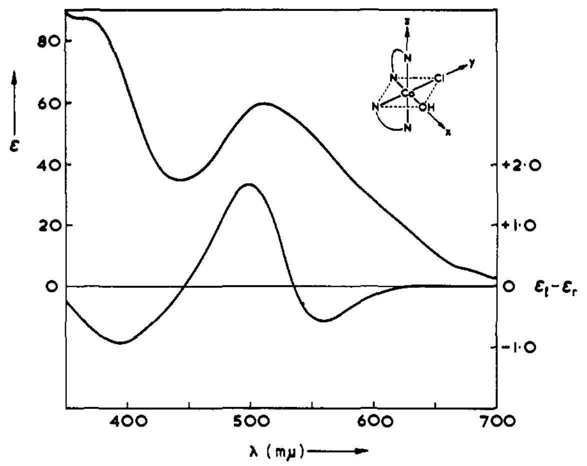

Figure 3. The equilibrium spectrum and circular dichroism of the ion *cis*-[Co(en)$_2$ClOH]$^+$, derived from the isomerization of *trans*-[Co(en)$_2$ClOH]$^+$, in L-2,3-butanediol. Shown schematically is the absolute configuration of the *cis*-[Co(en)$_2$ClOH]$^+$ asymmetrically synthesized in L-2,3-butanediol and the coordinate frame referred to in the text.

complexes show pronounced circular dichroism in the region of the d → d absorptions.[11]

In L-2,3-butanediol solution the complex *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride shows two circular dichroism bands of opposite sign in the 400–700-mμ region of the spectrum (Figure 2). Both bands are fairly weak but are easily detected because of the low intensity of the associated absorption. In the symbolism of the D_{4h} point group, the transition at about 600 mμ is the $^1A_{1g} \rightarrow {}^1E_g$ excitation[12] which carries 4 β units of transition angular momentum polarized in the directions of the nitrogen atom plane. The transition at around 450 mμ is the excitation[12] $^1A_{1g} \rightarrow {}^1A_{2g}$ whose transition angular momentum, $2\sqrt{2}\,\beta$ units, is polarized along the Cl–Co–Cl axis.

It is probable that the circular dichroism exhibited by the complex in the active solvent arises because the solvent preferentially constrains the ethylenediamine–cobalt rings into a particular dissymmetric conformation. This might occur by hydrogen bonding between the amine hydrogen atoms and the hydroxyl lone pairs of electrons of the solvent, so that the solvent may form a secondary chelate ring across an octahedral edge connecting nitrogen atoms of different ethylenediamine molecules.

The signs and intensity ratio of the two circular dichroic bands are very similar to those exhibited by *trans*-dichlorobis((−)-propylenediamine)cobalt(III) chloride,[11] and we suggest that the rings of the complex ion *trans*-[Co(en)$_2$Cl$_2$]$^+$ in L-2,3-butanediol are puckered in the same absolute configuration. This absolute configuration is shown in the inset of Figure 2.

Having ascribed the above mechanism for the appearance of optical activity in *trans*-[Co(en)$_2$Cl$_2$]$^+$ ion, we have categorized the phenomenon as an asymmetric transformation. The effect might be a case of asymmetric induction but we do not think this is so because amine systems such as *trans*-dichloro-1,4,8,11-tetraazacyclotetradecanecobalt(III), *trans*-[Co(cyclam)Cl$_2$]$^+$,[13] where the macrocyclic framework is incapable of conformational changes by hydrogen bonding show no optical activity when dissolved in the active solvent. In fact not all the *trans*-diacidobis(ethylenediamine)cobalt(III) complexes, and we have tried ten of these, show optical activity.

The analogous complexes, racemic *cis*-dichlorobis(ethylenediamine)cobalt(III) and racemic *cis*-dichlorobis(ethylenediamine)chromium(III), when freshly dissolved in L-2,3-butanediol show circular dichroism in the region of their d → d absorption bands. However, as we shall see in the next section, these two ions undergo asymmetric syntheses, and we are uncertain as to whether the activity is due to an asymmetric transformation of the chelate rings or due to the beginning of the process of asymmetric synthesis. If, in fact, an asymmetric transformation is being observed, the circular dichroic spectra are very similar to those of the resolved *cis* complexes.

III. Asymmetric Syntheses. In this section we describe four examples of asymmetric syntheses occurring in L-2,3-butanediol. It will be seen that the complexes are capable of complete resolution in this solvent.

1. The Isomerization and Resolution of the *trans*-Chlorohydroxobis(ethylenediamine)cobalt(III) Ion. The *trans*-chlorohydroxobis(ethylenediamine)cobalt(III) chloride monohydrate complex, *trans*-[Co(en)$_2$ClOH]Cl·H$_2$O, is insoluble in cold L-2,3-butanediol. If, however, the solution is slowly warmed to 70° over a period of 1 min, the complex dissolves completely to give a pink-violet solution. The visible absorption spectrum, shown in Figure 3, is almost identical with that of a carefully determined (see Experimental Section) spectrum of *cis*-[Co(en)$_2$ClOH]$_2$SO$_4$ in water–methanol solution. This observation leads us to suppose that, in the process immediately after dissolution, the complex ion *trans*-[Co(en)$_2$ClOH)$^+$ has almost completely

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[12] C. J. Ballhausen and W. Moffitt, *J. Inorg. Nucl. Chem.*, 3, 178 (1956).

[13] B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, 4, 1102 (1965).

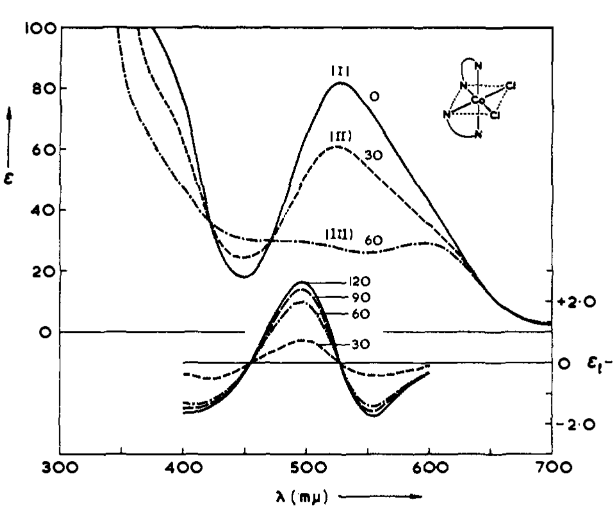

Figure 4. The absorption spectrum and associated circular dichroism of L-2,3-butanediol solutions of the ion *cis*-$[Co(en)_2Cl_2]^+$ at various time intervals. The numbers near the curves refer to the time the solutions were kept at 65°. In calculating the circular dichroism curves, the $\epsilon_l - \epsilon_r$ values were determined on the basis of the calculated concentrations of *cis*-$[Co(en)_2Cl_2]^+$ at any time and they, unlike the normal extinction coefficients (ϵ) in this figure, are not based on the total concentration of material. In the inset is shown schematically the absolute configuration of the *cis*-$[Co(en)_2Cl_2]^+$ ion synthesized in L-2,3-butanediol.

isomerized to the corresponding *cis*-$[Co(en)_2ClOH]^+$ isomer.

After the solution was allowed to cool to room temperature, the complex exhibited strong and constant circular dichroism in the region of the d → d absorption bands (Figure 3). The magnitude of the circular dichroism is as large as has been observed[14] for these *cis*-bis(ethylenediamine)cobalt(III) complexes which suggests that the *trans*-to-*cis* isomerism is complete and that total resolution has been achieved.

It will be seen that the absorption band at around 510 mμ, ascribed to the $^1A_{1g} \rightarrow {}^1T_{1g}$ magnetic dipole allowed excitation, is broad but shows little evidence of splitting. However, the negative and positive circular dichroism components under this band clearly show the splitting expected by the field of low symmetry produced by this complex. The semiempirical theory of Yamatera[15] allows us to assign these two circular dichroism bands derived from the $^1T_{1g}$ manifold. In the symbolism of the one-electron octahedral orbitals, which are not strictly appropriate in the present system, but are useful for the purposes of designation, the negative band at around 560 mμ is assigned to the excited state configuration $d_{xy}{}^1$, $d_{yz}{}^2$, $d_{xz}{}^2$, $d_{x^2-y^2}{}^1$. The hydroxyl group and the chloro group have similar ligand fields so that the other two excited configurations, $d_{xy}{}^2$, $d_{yz}{}^1$, $d_{xz}{}^2$, $d_{y^2-z^2}{}^1$ and $d_{xy}{}^2$, $d_{yz}{}^2$, $d_{xz}{}^1$, $d_{x^2-z^2}{}^1$ should be nearly degenerate and constitute the components of the positive band at around 500 mμ. These designations refer to the coordinate frame shown in the inset of Figure 3.

This particular sign pattern of the circular dichroism, under the $^1A_{1g} \rightarrow {}^1T_{1g}$ manifold, establishes[14,16] that the resolved complex ion *cis*-$[Co(en)_2ClOH]^+$, asymmetrically synthesized in L-2,3-butanediol, has the absolute configuration shown in the figure in the inset of Figure 3.

We do not know whether the conversion from *trans*-$[Co(en)_2ClOH]^+$ to *cis*-$[Co(en)_2ClOH]^+$ involves an intramolecular or an intermolecular process, but the latter process, involving the exchange of the labile[17] chloro group, seems more likely. Such a process would require, if the solvent does not coordinate, a five-coordinate intermediate which resembles either a square pyramid or a trigonal bipyramid. Although it is tempting to suggest that an optically active trigonal bipyramid is produced in the asymmetric isomerization, ways, perhaps excessively elaborate, can be envisaged by which a square-pyramidal intermediate can lead, in the active solvent, to a resolved product. Whatever the precise mechanisms involved for this and the following asymmetric syntheses, we are reasonably confident that hydrogen bonding between the amine hydrogen atoms and the solvent is involved because asymmetric syntheses do not occur in systems where there are no nitrogen hydrogen atoms, such as, for example, the bidentate arsine complexes.

2. The Isomerization and Resolution of the *cis*-Dichlorobis(ethylenediamine)cobalt(III) Ion.

A solution of racemic *cis*-dichlorobis(ethylenediamine)cobalt(III) tetraphenylborate in L-2,3-butanediol slowly isomerizes to give an equilibrium mixture of the *cis* and *trans* isomers. We have followed this process semiquantitatively in order to observe the gross features of the kinetic process. The reaction has been studied at 65°, and, at intervals of 30 min, the progress of the reaction has been analyzed spectrophotometrically as well as by circular dichroism. A typical example of such an analysis is shown in Figure 4.

It will be evident that the solution, in its approach to equilibrium, exhibits both a change in the absorption and in the circular dichroism spectrum. We calculate that after 30 min at 65° (curve II of the absorption spectrum, Figure 4) the solution contains 70% *trans*-$[Co(en)_2Cl_2]^+$ and 30% *cis*-$[Co(en)_2Cl_2]^+$ ions and that after 60 min, when the absorption spectrum has reached an essentially constant value and, presumably, the reaction has reached *cis–trans* equilibrium, there is 80% *trans*-$[Co(en)_2Cl_2]^+$ and 20% *cis*-$[Co(en)_2Cl_2]^+$. As can be seen from the circular dichroism, however, the solution has not reached chiral equilibrium until 2 hr has elapsed. The $\epsilon_l - \epsilon_r$ values in Figure 4 have been determined from the calculated concentrations of *cis*-$[Co(en)_2Cl_2]^+$ from the absorption spectrum at any time. The contribution to the circular dichroism from the *trans*-$[Co(en)_2Cl_2]^+$ is an order of magnitude less than that of the resolved *cis*-$[Co(en)_2Cl_2]^+$ complexes, and the curves are uncorrected for this small contribution.

As in the case of the *cis*-$[Co(en)_2OHCl]^+$ ion spectrum, the absorption band (curve I, Figure 4) at around 530 mμ is the magnetic dipole allowed transition $^1A_{1g} \rightarrow {}^1T_{1g}$ of the *cis*-$[Co(en)_2Cl_2]^+$ ion. In the essentially C_{2v} field of this ion, the degeneracy of the $^1T_{1g}$ upper state is removed into two components,[16] $^1A_1 \rightarrow {}^1A_1$, $^1B_2$ and $^1A_1 \rightarrow {}^1B_1$. A consideration[15,16] of the spectrochemical effects of the coordinated chloride ion and the ethylenediamine molecule leads to the assignment of the negative circular dichroism component at around 555 mμ as the $^1A_1 \rightarrow {}^1B_1$ transition and the positive circular

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[15] H. Yamatera, *Bull. Chem. Soc. Japan*, 31, 95 (1958).

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[17] R. G. Pearson, R. E. Meeker, and F. Basolo, *J. Am. Chem. Soc.*, 78, 2673 (1956).

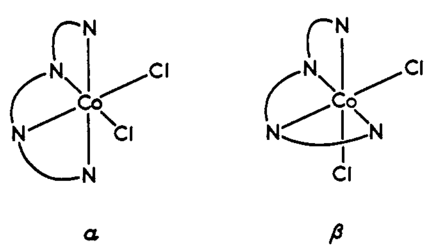

Figure 5. A schematic representation of the α and β isomers of *cis*-$[Co(trien)Cl_2]^+$ (trien = $H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$) in their respective absolute configurations that are synthesized in L-2,3-butanediol.

dichroism curve at around 495 mμ as the two-component ${}^1A_1 \rightarrow {}^1A_1, {}^1B_2$ transition. The absolute configuration[14,16] of the optically active ion *cis*-$[Co(en)_2Cl_2]^+$ synthesized in L-2,3-butanediol is therefore $P(C_2)$, the same as that of the *cis*-$[Co(en)_2ClOH]^+$ synthesized in L-2,3-butanediol, shown in the inset of Figure 4.

The kinetics of the *cis*-$[Co(en)_2Cl_2]^+$ ion in methanol solution have been thoroughly investigated. It has been shown that racemization and isomerization occur because of unimolecular chloride exchange[18] and that the intermediate must be five-coordinate because a six-coordinate methanolo intermediate is not sufficiently reactive to account for the chloride exchange.[19] It seems probable that the *cis*-$[Co(en)_2Cl_2]^+$ ion in L-2,3-butanediol reacts by way of a similar mechanism. But whereas the process of racemization in methanol involves the production of the enantiomorphs in equal numbers, the reaction in L-2,3-butanediol, whether we refer to the macrochemical observation or the microchemical processes, involves the time reversal of the racemization process. Hence we call the chiral reaction, of the *cis*-$[Co(en)_2Cl_2]^+$ ion in L-2,3-butanediol, *antiracemization.*

The unimolecular antiracemization reaction may be written

$$dl\text{-}cis\text{-}[Co(en)_2Cl_2]^+ \xrightarrow{k_1} [Co(en)_2Cl\cdot]^{2+} + Cl^- \xrightarrow{k_2} d\text{-}cis\text{-}[Co(en)_2Cl_2]^+$$

where k_1 is the rate-determining step. Such a reaction scheme poses the perhaps interesting question as to whether the chirality of the over-all reaction is imparted at the first (k_1) or second (k_2) or both stages of the reaction. This question might be resolved by isotopic chloride exchange experiments. So far, we know only that the over-all rate constant for the production of one antipode is greater than the over-all rate constant for the production of the other antipode.

3. The Isomerization and Resolution of the *cis*-Dichlorotriethylenetetraminecobalt(III) Ion. The complex ion *cis*-dichlorotriethylenetetraminecobalt(III), *cis*-$[Co(trien)Cl_2]^+$, may exist in two isomeric forms both of which satisfy the topological conditions required for optical activity. These two forms called α and β are shown in Figure 5. Both isomers have been isolated, characterized, and resolved into their individual optical antipodes. In addition the relationship between their circular dichroism and their absolute configuration is known.[20] The first absorption band, ${}^1A_{1g} \rightarrow {}^1T_{1g}$, of the α isomer is somewhat broader than, and displaced slightly to longer wavelengths from, the corresponding band of the β isomer. In the range 400–650 mμ the α isomer, having the absolute configuration shown in Figure 5, has three circular dichroism bands: a negative band at around 590 mμ ($\epsilon_l - \epsilon_r(\max) \approx -1.8$), a positive band at around 530 mμ ($\epsilon_l - \epsilon_r(\max) \approx +2.8$), and a weaker positive band at around 420 mμ ($\epsilon_l - \epsilon_r(\max) \approx +0.3$). The absolute configuration of the β isomer as shown in Figure 5 has, in the range 400–500 mμ, two negative circular dichroism bands: one at around 570 mμ ($\epsilon_l - \epsilon_r(\max) \approx -0.7$) and one at around 470 mμ ($\epsilon_l - \epsilon_r(\max) \approx -0.2$).

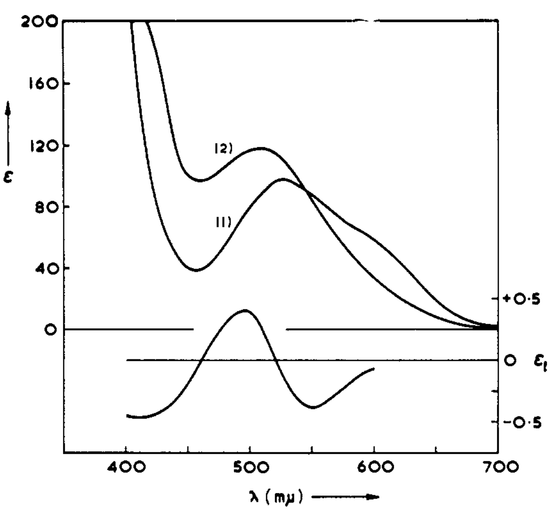

Figure 6. Curve 1 represents the visible absorption spectrum of a freshly prepared solution of α-*cis*-$[Co(trien)Cl_2]^+$ ion in L-2,3-butanediol, and curve 2 is the equilibrium spectrum after this solution had remained at 65° for about 2 hr. The circular dichroism curve is that observed of the equilibrated solution and is calculated on the basis of the bulk concentration of the material.

When racemic α-*cis*-dichlorotriethylenetetraminecobalt(III) tetraphenylborate, dissolved in L-2,3-butanediol, is heated at 65°, a slow reaction occurs which can be detected by a change in the visible absorption spectrum (Figure 6). The shape and position of the first absorption band of the equilibrated solution is consistent with the assumption that the α isomer has partly isomerized to the β isomer. This assumption is confirmed by the nature of the circular dichroism change which accompanies the spectral change. After about 2 hr at 65° the α-*cis*-$[Co(trien)Cl_2]^+$ isomerizes to an equilibrium mixture which shows the circular dichroism curve in Figure 6. It will be noted that the signs of the circular dichroism bands at 550 and 445 mμ are those expected for the α isomer in the absolute configuration of Figure 5, and, were this the only isomer present in the solution, the band at 410 mμ should be positive. The fact that the 410-mμ circular dichroism band is negative establishes, consistent with the absorption spectrum change, the presence of the β isomer having the absolute configuration shown in Figure 5. It should be mentioned that the claim by Sargeson and Searle[20] to have resolved totally the β-*cis*-$[Co(trien)Cl_2]^+$ ion is probably mistaken since, if we have interpreted our results correctly, the resultant equilibrium mixture circular dichroism curve at around 420 mμ is twice as intense as that reported for the pure β isomer.

The kinetic and mechanistic remarks made about the *cis*-$[Co(en)_2Cl_2]^+$ and *cis*-$[Co(en)_2ClOH]^+$ systems probably apply to the antiracemization and isomerization processes that occur in the present system where, it will

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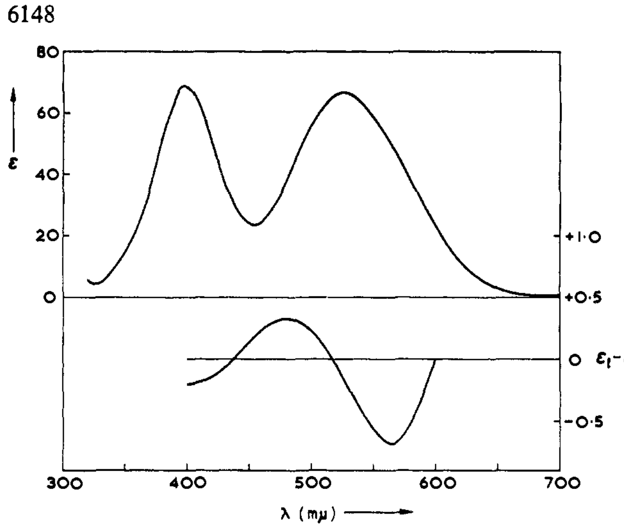

Figure 7. The visible absorption spectrum of a freshly prepared L-2,3-butanediol solution of the ion *cis*-$[Cr(en)_2Cl_2]^+$ and the circular dichroism obtained after this solution was heated at 65° for 30 min.

be noted, the absolute configurations of the α and β isomers, equilibrated in active 2,3-butanediol, are related by an edge displacement of the terminal ethylamine linkage.

4. The Asymmetric Synthesis of the *cis*-Dichlorobis(ethylenediamine)chromium(III) Ion. In the previous asymmetric syntheses it was shown that the absolute configurations of the products *cis*-$[Co(en)_2ClOH]^+$ and *cis*-$[Co(en)_2Cl_2]^+$ were the same. This suggests that the absolute configurations of *cis*-bisethylenediamine complexes might be interconnected by the use of the optically active solvent. Of particular interest is the connection between the tervalent cobalt- and tervalent chromium-*cis*-bisethylenediamine systems, where in the latter it has been tacitly assumed[14,16] that the relationship between the absolute configuration and the circular dichroism is the same as that for the analogous cobalt complexes. We therefore include the result of the asymmetric syntheses of *cis*-dichlorobis(ethylenediamine)chromium(III) tetraphenylborate, *cis*-$[Cr(en)_2Cl_2]BPh_4$, in L-2,3-butanediol.

At 65° the racemic *cis*-$[Cr(en)_2Cl_2]^+$ ion dissolved in L-2,3-butanediol antiracemizes, but after about 30 min at this temperature, the solution develops a cloudy colloidal suspension characteristic of the products formed in the decomposition of chromium–amine complexes in water and alcohols. In Figure 7 we show the absorption spectrum of a freshly prepared solution of the *cis*-$[Cr(en)_2Cl_2]^+$ ion and also the associated circular dichroism of the ion after about 30 min of antiracemization at 65° in L-2,3-butanediol.

The first spin-allowed transition of octahedral chromium(III) ($^4A_{2g} \rightarrow {}^4T_{2g}$) is magnetic dipole allowed and, in the *cis*-$[Cr(en)_2Cl_2]^+$ ion, should split into the same pattern as the corresponding *cis*-$[Co(en)_2Cl_2]^+$ ion. It will be seen that the band at around 525 mμ carries a similar circular dichroism structure as the $P(C_2)$ *cis*-$[Co(en)_2Cl_2]^+$ ion. Since it seems reasonable to assume that, in L-2,3-butanediol, both the chromium and cobalt systems will be induced to antiracemize by a similar mechanism, it is probable that the present result supports the supposition that analogous chromium and cobalt systems will have similar circular dichroism for the same absolute configuration.

Discussion

In the course of this investigation we have used a variety of organic and inorganic compounds dissolved in optically active solvents in order to observe the chiral effects described in this note. Among the solvents used were (−)-3-heptanol, diethyl D-tartrate, (−)-1,2-diaminopropane, α-pinene, and pinane, but in none of these cases, except that biphenyl is probably asymmetrically transformed in pinane, were the chiral interactions detectable. However, in all cases the active solvents must, to some extent, asymmetrically perturb the solutes, and the fact that L-2,3-butanediol shows such pronounced chiral effects must be due to the particular stability and intensity of the solute–solvent interaction. We do not know what particular properties of L-2,3-butanediol distinguish it from the other solvents, but we are reasonably convinced that its hydrogen-bonding properties are important.

The recent derivation of a dissymmetric dispersion formula[21] indicates that dissymmetric interaction is a general phenomenon in optically active systems. Like ordinary dispersion forces, the dissymmetric dispersion forces depend on the sums of the rotational strengths of all the transitions of the system and inversely to the squared difference in energy of the excited and ground states. In the present systems, calculation shows that the chiral free-energy difference obtained from dispersion forces is insufficiently large to account for the effects observed. They, however, may be of paramount importance in contributing to the crystal packing forces of molecules containing inherently dissymmetric chromophores such as, for example, hexahelicene.

Finally, it is perhaps relevant to point out that the results recorded here may bear some resemblance to the asymmetric syntheses which appear to be the natural occurrence of biological systems.

Experimental Section

The compounds *trans*-$[Co(en)_2Cl_2]Cl$, *trans*-$[Co(en)_2OHCl]Cl \cdot H_2O$, *cis*-$[Co(en)_2Cl_2]Cl$, and *cis*-$[Cr(en)_2Cl_2]Cl$ were made by the methods of Werner.[22] Basolo's[23] method was used for the preparation of α-*cis*-$[Co(trien)Cl_2]Cl$. Conversion of the appropriate compounds to their tetraphenylboron salts was accomplished by methods described previously.[18] The spectrum of the *cis*-$[Co(en)_2OHCl]^+$ ion has not been recorded in water because of the ready hydrolysis[17] of the coordinated chloro group. We have been able to obtain a "constant" spectrum in 50% aqueous methanol by the following method. The aquo complex,[22] *cis*-$[Co(en)_2ClH_2O]SO_4 \cdot H_2O$, was dissolved in water and methanol added to make a 50% aqueous solution. The visible spectrum of this solution was similar to that of an aqueous solution of the *cis*-chloroaquo ion. On the careful addition of 2,6-lutidine to the methanol–water solution, the spectrum immediately changed to one which was sufficiently constant and very similar, as far as intensity and position of the visible absorption peaks were concerned, to that recorded in Figure 3 of *cis*-$[Co(en)_2OHCl]^+$ in L-2,3-butanediol.

Commercial benzil was recrystallized twice from ethanol while benzophenone was used without further purification.

The solvent L-2,3-butanediol was obtained from Lights, who produced it biologically.[24] A neat sample of L-2,3-butanediol in a 10-cm tube rotated a plane polarized sodium D-line beam −12.72°.

The absorption spectra were measured with a Unicam S.P.800 B recording spectrophotometer, and the circular dichroism spectra were obtained by a Roussel-Jouan Dichrographe which had a sensitivity of 1.5×10^{-4}.

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