A Regional Rule for the Optical Activity of Conformational Isomers of Octahedral Transition Metal Complexes

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Abstract: Experimentally based intuitive arguments are presented which arrive at a regional rule for the optical activity of the d–d transitions of the conformational isomers of octahedral metal complexes. The space demarcation derived is shown to correspond to the simplest pseudoscalar representation of the O_h point group. For polyamine complexes three general sources of dissymmetry are recognized: the effect of the dissymmetric arrangement of the alkyl groups, the effects of dissymmetrically arranged amino hydrogen atoms, and the effects of dissymmetric distortions of the donor atoms. It is suggested that the first and last of these effects are of comparable magnitude and are generally opposed in sign. The spin-paired d^6 cobalt(III) systems are used as examples although the arguments are applicable to all d-electron configurations. The origin of the sign of the optical activity for the three components of the first magnetic dipole allowed transition is discussed in detail and an explanation is offered in terms of the orientations of the relevant orbitals involved in the three components of this transition with respect to the disposition of the various groups around the metal. It is concluded that the number of variables of uncertain magnitude involved in the application of the rule precludes any ready applicability, though it does provide a basis for interpretation. It is shown that solution circular dichroism spectra are unreliable for obtaining "hypothetical gas" spectra because solvation effects cause inversions of sign. Solid-state spectra appear to give the best approximation to the environmentally free spectrum. The absolute configuration of (−)-stilbenediamine has been assigned from equilibration studies of the two isomers of the $[Co(-)(stien)_3]^{3+}$ ion, and it is noted that the *trans*-[Co*R*,*R*-$(stien)_2Cl_2]^+$ ion has an inverted circular dichroism spectrum compared to analogous compounds. Methods for the preparation, separation of the geometric isomers, and resolution of the optical isomers of 2,4-diaminopentane are given and the preparation and characterization of other relevant complexes are described.

The optical activity shown by the d–d electronic excitations of transition metal ions has been ascribed conceptually to three types of origin. The first is the configurational contribution which is caused by the dissymmetric orientation of the chelate rings about a metal ion. This effect is the classical view of dissymmetric coordination compounds and engenders optical activity in the d–d transitions of such complexes as the trioxalatocobaltate(III) ion and the tris(ethylenediamine)-cobalt(III) ion. In the latter, unlike the former, there is a second source of asymmetry which appears because of the circumstance that the ethylenediamine rings are in puckered dissymmetric conformations. This effect is called the conformational effect and can exist simultaneously with or independently of the generally larger configurational effect. The last, and probably the weakest effect, is the vicinal effect which arises from the presence of asymmetric groups on the chelate rings. In general, for five-membered saturated ring systems the vicinal and conformational effects are contingent phenomena, the asymmetry of one determining the other.[1] However, systems can be envisioned where the vicinal and conformational effects are independent; for example, the chelate ring formed by the active 1,3-diaminobutane ligand in the chair conformation has only a vicinal contribution. It should be pointed out, however, that although these characterizations are convenient and appear to have a reasonable experimental basis for differentiation, systems occur where formally none of these effects seems to exist and yet the total complex is optically active.[2]

This paper is concerned with the optical activity shown by the d–d transitions of metal complexes which owe their activity only to the conformational and vicinal effects. The final object is to explore the possibility of enunciating a general regional rule, in terms of the areas of space occupied by the ligand atoms about the metal ion, from which, by knowing the nonabsolute conformations of the chelate rings, one may predict their absolute configurations from the sign of the circular dichroism shown by particular d–d bands. We proceed in this object by first considering a number of partly intuitive principles.

(1) The Dissymmetric Space

Let us suppose that we have a single puckered unsubstituted five-membered chelate ring involving a transition metal ion where the only source of asymmetry is the puckering of this ring. And suppose further that the circular dichroism of the d–d bands arises solely from dissymmetric interactions between the electrons and nuclei of the dissymmetrically oriented ligand and the d electrons of the metal. For the present we shall assume the donor atoms to be positioned exactly at the two octahedral vertices. Perhaps the closest physical analogy to the above situation is a chelate ring formed by the 1,2-ethanedithiolate ligand. Under these conditions the optical activity would arise solely from the dissymmetric potential exerted by the CH_2 groups of the ligand. The argument which follows may, for simplicity, be perceived in terms of this system, although it is applicable to all five- or six-membered chelate rings.

Suppose it is found experimentally that the λ conformation of the ring produces positive circular dichroism for a particular *single* d–d transition; then it is certain that the (mirror image) δ ring conformation will produce equal negative circular dichroism for the same transition. It is also evident that were the ring forced

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(1) E. J. Corey and J. C. Bailar, *J. Amer. Chem. Soc.*, **81**, 2620 (1959).
(2) F. R. Keene, G. H. Searle, and S. F. Mason, *Chem. Commun.*, 893 (1970).

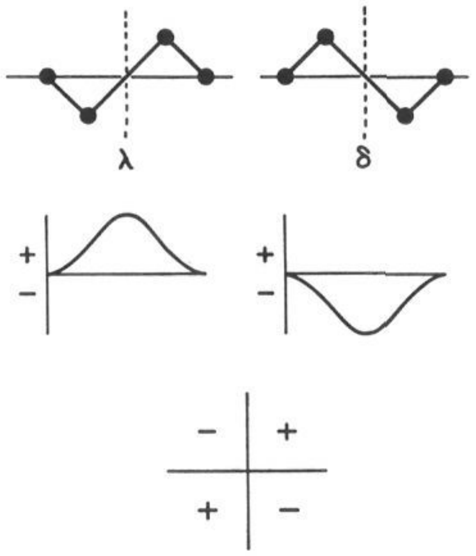

Figure 1. The λ and δ conformations of a five-membered chelate ring and the corresponding circular dichroism assumed to be associated with them which leads to the quadrant rule for an octahedral edge.

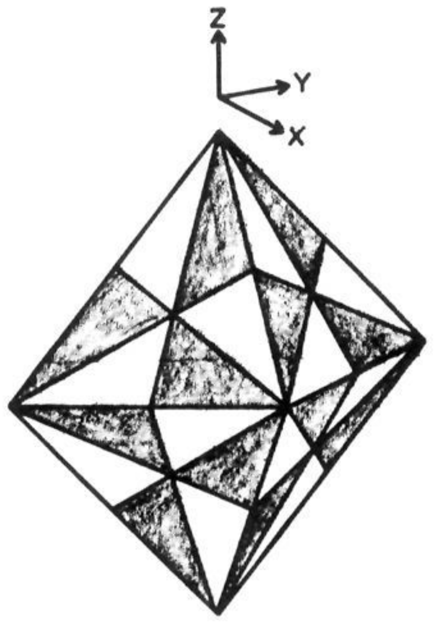

Figure 2. The simplest (repulsive) pseudoscalar potential for the O_h point group.

to adopt a (strained) planar conformation the optical activity would vanish, appearing again for infinitesimal displacements of the CH_2 groups away from the octahedral edge (the line joining the donor atoms). Thus an octahedral edge represents a node in the dissymmetric potential. In addition, since the CH_2 groups generate positive circular dichroism when they are positioned to the "bottom left" and "top right" (λ ring) and give negative circular dichroism when they are positioned to the "top left" and "bottom right" (δ ring) of the octahedral edge, it suggests that a second node exists normal to the octahedral edge and coincident with the twofold axis. Figure 1 shows the argument diagrammatically. Thus, on this basis, we would conclude that an octahedral edge must have the elements of a quadrant rule to accommodate the optical activity generated by a puckered five-membered chelate ring. The choice of an octahedral edge is arbitrary, and the above argument should be equally applicable to all 12 edges. There is experimental evidence to support this assumption. Thus the conformational contribution to the intensity of the circular dichroism of the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition of the series of complex ions $[Co(-)pn(NH_3)_4]^{3+}$, *trans*-$[Co(-)(pn)_2(NH_3)_2]^{3+}$, $[Co(-)(pn)_2en]^{3+}$, and $[Co(-)(pn)_3]^{3+}$ ((−)pn = (−)-propylenediamine, en = ethylenediamine) lies approximately in the ratio 1:2:2:3, respectively.[3] This implies that the conformational contributions from the rings are additive and independent of which edge they occupy, as would be required by our assumption that all 12 edges are equivalent and the circular dichroism is generated by a single dissymmetric potential. A space divided equivalently about an octahedron which makes each edge have the properties of a quadrant rule is the dissymmetric delineation shown in Figure 2. A CH_2 group occupying the shaded regions will contribute positive circular dichroism and negative circular dichroism in the unshaded regions, based on our assumption that the λ ring generates positive circular dichroism. (Of course if the opposite were found to be the case, the shaded and unshaded regions would be interchanged.)

This intuitively derived result is interesting, since the demarcated object in Figure 2, with its 48 sectors and 9 nodal planes, is invariant with respect to primary operations (pure rotations), and changes sign for all secondary operations (inversions, planes, and improper rotations) and transforms as the lowest pseudoscalar representation, A_{1u} of O_h. It is precisely the dissymmetric space delineation one would derive formally if one assumed that optical activity was produced by a (pseudoscalar) potential superimposed on a molecule with essentially O_h symmetry.[4] The algebraic Cartesian form of the function is $-XYZ[X^4(Y^2 - Z^2) + Y^4(Z^2 - X^2) + Z^4(X^2 - Y^2)]$. It should be noted if the potential were attractive, the function would have a positive sign in front and would reverse the sign of the shaded and unshaded areas in Figure 2; the negative sign in front of the function indicates a repulsive potential. The function has a sharply varying dependence with distance r, namely r^{-19}, indicating that the optical activity will attenuate rapidly as the asymmetric perturber is removed from the central atom. This dependence alone, however, does not imply that one can always neglect contributions from dissymmetrically disposed groups even if they are outside the coordination sphere.[5] It is perhaps pertinent to add that, from a purely geometric point of view, the regional conformational dissymmetry of many complexes can be accounted for in terms of much simpler pseudoscalar potentials. As examples, the $[Co(-)pn(NH_3)_4]^{3+}$ ion's dissymmetry can be represented by a quadrant rule (XY), whereas that of *trans*-$[Co((-)pn)_2(NH_3)_2]^{3+}$ can be represented by an octant rule (XYZ), where in both cases the X and Y axes are oriented between the donor atoms. However, the XY function has a r^{-5} distance dependence, whereas the XYZ function has a r^{-7} dependence, and since the pn ligands are at similar distances from the cobalt atom, we would not expect the observed[3] additivity per ring of the circular dichroism if these two potentials applied respectively for the two systems. This we take to imply a single pseudoscalar potential for all octahedral systems.

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[3] B. E. Douglas, *Inorg. Chem.*, **4**, 1813 (1965); S. F. Mason, A. M. Sargeson, R. Larsson, B. J. Norman, A. J. McCaffery, and G. M. Searle, *Inorg. Nucl. Chem. Lett.*, **2**, 333 (1966); *J. Chem. Soc.*, 1304, 1310 (1968); K. Ogino, K. Murano, and J. Fujita, *Inorg. Nucl. Chem. Lett.*, **4**, 351 (1968).

[4] S. Sugano, *J. Chem. Phys.*, **33**, 1883 (1960); N. K. Hamer, *Mol. Phys.*, **5**, 339 (1962); H. Poulet, *J. Chim. Phys. Physicochim. Biol.*, **59**, 584 (1962); J. A. Schellman, *J. Chem. Phys.*, **44**, 55 (1966); F. S. Richardson, *J. Phys. Chem.*, **75**, 692 (1971).

[5] B. Bosnich and J. MacB. Harrowfield, *J. Amer. Chem. Soc.*, **93**, 4086 (1971).

(2) The Polyamine Systems

The above arguments assumed an idealized system with a single source of dissymmetric perturbation, and real systems are generally more complicated, although they can be fitted into the present framework. The puckered ethylenediamine metal ring system is a case in point, where more than just the influence of the alkyl groups can generate the optical activity. Crystal structures of these systems show that the N–M–N angle is less than 90° (about 86–87°) and that the nitrogen atoms are skewed, one lying above and the other below the idealized octahedral edge. Figure 3 shows these displacements, which may be calculated from the structure of *trans*-$[Co(-)(pn)_2Cl_2]Cl \cdot 2H_2O \cdot HCl$.[6] Each nitrogen atom is skewed away from the mean plane by about 0.1 Å. This is a common and general observation and provides a second source of asymmetry in these systems.

It is clear that the nitrogen atoms lie largely in sectors of the pseudoscalar potential which are opposed in sign to the sectors occupied by the alkyl groups, and in order to proceed we require not only a rough estimate of the relative magnitudes but also the signs of these effects. From a theoretical standpoint, the sign of the interaction depends to some extent on the model chosen for the nature of the potential and the approximations used to describe it. Broadly, there are three types of potential which are generally considered, the static,[7] the dynamic,[8] and exchange interactions, all of which in any given system can contribute to optical activity; and at any given distance of perturbation the sign of interaction of any one mechanism will not necessarily be the same as the others.[9] In the present systems, probably all three mechanisms contribute, but whatever the origins of the dissymmetric potential the basic symmetry arguments employed here will remain valid. We know of none and have not been able to obtain any unambiguous experimental evidence which determines the signs of these interactions in metal complexes; but because it appears to provide a self-consistent rationalization of the results obtained, we assume that both the alkyl groups and the donor nitrogen atoms will have a net repulsive effect on the d electrons. If this is so, the alkyl groups and the donor nitrogen atoms will generally oppose each other in contributing to the optical activity. There is some experimental evidence which suggests that these two effects are of roughly comparable magnitude, despite the fact that the nitrogen atoms lie closer to the d electrons than the alkyl groups. Thus the *trans*-$[Co(dien)_2]^{3+}$ ion (dien = $(NH_2CH_2CH_2)_2NH$),[2] the *trans*-$[PdCl_4Am_2]$ (Am = (−)-phenylethylamine),[10] and the series of complexes $[Co(NH_3)_5\text{-L-amino acid}]^{2+}$ [11] all show roughly comparable circular dichroism. The first compound formally has little or no configurational, conformational or vicinal contribution, and presumably the circular dichroism is produced by dissymmetric distortions of the donor atoms; the rest of the complexes presumably have no or little distortions of their donor atoms, and it seems that the circular dichroism is produced by dissymmetric interactions of the substituent groups. If one views these results in relation to the sharp r^{-19} dependence of the O_h potential, one might suppose that nearly all the circular dichroism would be generated by dissymmetric donor group distortions. However, the nodal planes of the octahedral potential converge to the extrema of the metal–ligand bonds, so that for small distortions, the donor atoms will extend over a number of sectors of opposing sign which will lead to cancellation of the circular dichroism. This is shown pictorially in Figure 3. The alkyl groups also tend to overlap sectors, but because they are further away, their orientation with respect to sectors is less ambiguously defined.

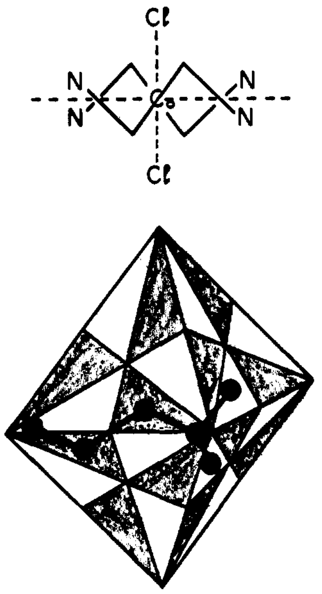

Figure 3. The distortions in the *trans*-$[CoR(pn)_2Cl_2]^+$ ion, where the dotted line represents the mean CoN_4 plane, and the sector occupancy of the atoms of an N-substituted ethylenediamine ring in the pseudoscalar potential.

There is one further complication in the amine systems which requires consideration, and this concerns the hydrogen atoms of the donor groups. In general, both axial and equatorial hydrogen atoms (or other substituents on the nitrogen atoms) lie mainly in sectors which are opposite in sign to the sectors occupied by the CH_2 groups, although free equatorial groups may lie close to a nodal plane (Figure 3). We have no evidence for the sign of the potential of these hydrogen atoms. The sign may well vary with the polarity of the N–H bond, giving opposing potentials depending on the electron-releasing or -withdrawing properties of the metal and the substituents on the chelate ring. Whatever the sign, the hydrogen atoms do not appear to have a dominating influence on the circular dichroism of the systems we discuss here.

It will be noted that the O_h potential does not distinguish between conformational and vicinal effects as such, since asymmetric groups, in the same way as conformations, contribute to the circular dichroism according to the sector of the potential which embraces them. Should it be shown that chelate rings which lie exactly along or are distorted exactly along octahedral

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(6) A. Nakahara, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Jap.*, **25**, 331 (1952).

(7) W. J. Kauzmann, J. E. Walter, and H. Eyring, *Chem. Rev.*, **27**, 339 (1940); T. D. Bouman and A. Moscowitz, *J. Chem. Phys.*, **48**, 3113 (1968).

(8) J. G. Kirkwood, *ibid.*, **5**, 479 (1937); E. G. Holm and O. E. Weigang, *ibid.*, **48**, 1127 (1968).

(9) H. Eyring, H. C. Lin, and D. Caldwell, *Chem. Rev.*, **68**, 525 (1968).

(10) B. Bosnich, *J. Chem. Soc. A*, 1394 (1966).

(11) C. J. Hawkins and P. J. Lawson, *Inorg. Chem.*, **9**, 6 (1970).

Chart I

$$\begin{array}{l}
(\mathrm{d}_{xz})^2 \left\{\frac{1}{\sqrt{2}}(\mathrm{d}_{xz} + \mathrm{d}_{yz})\right\}^2 \left\{\frac{1}{\sqrt{2}}(\mathrm{d}_{xz} - \mathrm{d}_{yz})\right\}^2 : \quad {}^1\mathrm{A}(C_2);\ {}^1\mathrm{A}_1(D_2);\ {}^1\mathrm{A}_{1g}(D_{4h});\ {}^1\mathrm{A}_{1g}(O_h) \\
\left.\begin{array}{l}
(\mathrm{d}_{xy}) \left\{\frac{1}{\sqrt{2}}(\mathrm{d}_{xz} + \mathrm{d}_{yz})\right\}^2 \left\{\frac{1}{\sqrt{2}}(\mathrm{d}_{xz} - \mathrm{d}_{yz})\right\}^2 (\mathrm{d}_{x^2-y^2}): \quad {}^1\mathrm{B}(C_2);\ {}^1\mathrm{B}_1(D_2);\ {}^1\mathrm{A}_{2g}(D_{4h}) \\
\left.\begin{array}{l}
(\mathrm{d}_{xy})^2 \left\{\frac{1}{\sqrt{2}}(\mathrm{d}_{xz} + \mathrm{d}_{yz})\right\} \left\{\frac{1}{\sqrt{2}}(\mathrm{d}_{xz} - \mathrm{d}_{yz})\right\}^2 (\mathrm{d}_{x^2-y^2}): \quad {}^1\mathrm{A}(C_2);\ {}^1\mathrm{B}_2(D_2) \\
(\mathrm{d}_{xy})^2 \left\{\frac{1}{\sqrt{2}}(\mathrm{d}_{xz} + \mathrm{d}_{yz})\right\}^2 \left\{\frac{1}{\sqrt{2}}(\mathrm{d}_{xz} - \mathrm{d}_{yz})\right\} (\mathrm{d}_{x^2-y^2}): \quad {}^1\mathrm{B}(C_2);\ {}^1\mathrm{B}_3(D_2)
\end{array}\right\} {}^1\mathrm{E}_g(D_{4h})
\end{array}\right\} {}^1\mathrm{T}_{1g}(O_h)
\end{array}$$

edges contribute to the optical activity, then the present potential cannot accommodate this configurational effect, since octahedral edges represent nodes in the potential. Presumably, this effect would require a lower order potential for its explanation. Finally, it will be evident in systems with nonaxially symmetrical groups *e.g.*, N_3^-, NCS^-, NO_2^-, NO_3^- etc., that the chiral orientations of these groups can contribute to the optical activity. Indeed, as we shall show elsewhere, these effects appear in some cases to dominate the circular dichroism. For this reason we shall restrict the discussion here to molecules with axially symmetrical groups.

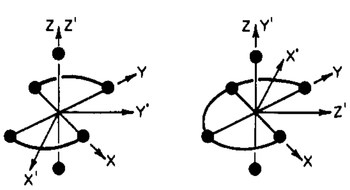

Figure 4. The octahedral coordinates (x, y, z) and the coordinates (x', y', z') for the D_2 and C_2 point groups.

(3) Electronic Considerations

We are here concerned specifically with spin-paired Co(III) complexes, and the discussion which follows is confined to the electronic properties of these complexes, although it is a trivial matter to extend it to other electron configurations. Further, we shall concern ourselves mainly with the first spin-allowed transition, ${}^1A_{1g} \rightarrow {}^1T_{1g}$, because, first, it is not usually overlapped by charge-transfer bands and, second, because of its zero-order magnetic dipole character, it is expected to show stronger circular dichroism than the ${}^1A_{1g} \rightarrow {}^1T_{2g}$ excitation.[12] Most of the complexes discussed have the *trans*-$[Co(N)_4(X)_2]^{n+}$ chromophore which, to the donor group approximation, will cause the upper ${}^1T_{1g}$ state to split into a ${}^1A_{2g}$ state, remaining at the absorption energy of the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition of the $[Co(N)_6]^{3+}$ chromophore, and a ${}^1E_g$ state, displaced in energy halfway between the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition energies of the $[Co(N)_6]^{3+}$ and $[Co(X)_6]^{n+}$ chromophores.[13] Thus, any proper interpretation of the circular dichroism of the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition must consider all three components which in many complexes have different signs.[14] It is clear that a single pseudoscalar potential must apply for all three components whether or not they carry circular dichroism of opposing sign. It is to this problem that we now address ourselves by considering the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ orbital functions more closely.

The (O_h) ground-state ${}^1A_{1g}$ function is $(d_{xy})^2(d_{xz})^2(d_{yz})^2$ while the (triply) degenerate ${}^1T_{1g}$ excited state functions may be written in the following orbital form

$$(d_{xy})(d_{xz})^2(d_{yz})^2(d_{x^2-y^2})$$
$$(d_{xy})^2(d_{xz})(d_{yz})^2(d_{z^2-x^2})$$
$$(d_{xy})^2(d_{xz})^2(d_{yz})(d_{y^2-z^2})$$

where the necessary antisymmetry is understood. In lower symmetry point groups, these functions become mixed within themselves and with other functions of the same symmetry. We shall only consider approximate wave functions formed by mixing within the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ orbital manifold. The justification for this procedure rests on the assumption, generally supported by experiment, that the characteristics of the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition are largely retained in the lower point groups.

We consider as examples the two complex ions *trans*-$[Co(-)(bn)_2Cl_2]^+$ and active *trans*-$[Co(trien)Cl_2]^+$, where $(-)$bn = $(-)$-2,3-butanediamine and trien = triethylenetetramine, which belong to the point groups D_2 and C_2, respectively. The D_2 and C_2 perturbations, superimposed on the D_{4h} perturbation, arise first from the donor atom distortions and probably to a lesser extent from the presence of the connecting atoms of the chelate rings. We now define a new set of functions, in terms of the original octahedral set, which span the irreducible representations of the point groups D_2 and C_2. The original and new axis frames are shown in Figure 4, where the x' and y' axes in the *trans*-$[Co(trien)Cl_2]^+$ ion are defined in recognition of the fact that the major first-order perturbation arises from the D_{4h} field. Within the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ manifold, the new (approximate) functions become those shown in Chart I.

Hereinafter the two orbitals $(1/\sqrt{2})(d_{xz} + d_{yz})$ and $(1/\sqrt{2})(d_{xz} - d_{yz})$ are labeled d_{xz+yz} and d_{xz-yz}, respectively. The result of the new quantization is to rotate the d_{xz} and d_{yz} by 45° about the z axis, where the d_{xz+yz} is oriented in the z', y' plane and the d_{xz-yz} orbital is oriented in the x', y' (C_2), x', z' (D_2) plane.[15] The differing orientations of these two orbitals and the others provide a basis for our interpretation of the varying signs of the circular dichroism observed associated with the ${}^1T_{1g}$ manifold.

(4) Absolute Configurations

This paper describes the circular dichroism of the following complex ions: *trans*-$[CoR(pn)_2Cl_2]^+$, *trans*-

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(12) W. Moffit, *J. Chem. Phys.*, **25**, 1189 (1956).

(13) H. Yamatera, *Bull. Chem. Soc. Jap.*, 31, 95 (1958).

(14) C. J. Hawkins, "Absolute Configuration of Metal Complexes," F. A. Cotton and G. Wilkinson, Ed., Interscience, New York, N. Y., 1971, pp 202–209.

(15) For diagrams, see B. N. Figgis, M. Gerloch and R. Mason, *Proc. Roy. Soc., Ser. A*, **309**, 91 (1969).

(Cl)-[Co*R*(pn)(NH$_3$)$_2$Cl$_2$]$^+$, *trans*-[Co*R*,*R*(chxn)$_2$Cl$_2$]$^+$, *trans*-[Co*R*,*R*(bn)$_2$Cl$_2$]$^+$, *trans*-[Co*R*,*R*(stien)$_2$Cl$_2$]$^+$, *trans*-[Co*R*,*R*(dmtn)$_2$Cl$_2$]$^+$, *trans*-*S*,*S*-[Co-2,3,2-tetCl$_2$]$^+$, *trans*-*R*,*R*-[Co(trien)Cl$_2$]$^+$, and *trans*,*trans*-*S*,*S*-[Co(*N*-Meen)$_2$-Cl$_2$]$^+$. The abbreviations have the following meanings: *R*pn = (−)-propylenediamine, *R*,*R*chxn = (−)-*trans*-1,2-cyclohexanediamine, *R*,*R*bn = (−)2,3-butanediamine, *R*,*R*stien = (−)-stilbenediamine, *R*,*R*dmtn = (−)-2,4-pentanediamine, 2,3,2-tet = $NH_2CH_2CH_2NHCH_2CH_2CH_2NHCH_2CH_2NH_2$, trien = $NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$, and *N*-Meen = *N*-methylethylenediamine. Absolute crystal structure determinations have established the configurations of *R*pn,[16] *R*,*R*chxn[17,18] and *trans*,*trans*-[Co(*N*-Meen)$_2$-Cl$_2$]$^+$,[19] while the absolute configurations of *R*,*R*bn[20] and *trans*-*R*,*R*-[Co(trien)Cl$_2$]$^+$ [21] have been established unambiguously by chemical correlations. The absolute configuration of dmtn has not been established and the *R*,*R* assignment is based on largely unproven circumstantial evidence;[22] the point we wish to make about the complex of this ligand, however, is not dependent upon the knowledge of its absolute configuration.

The absolute configuration of (−)-stien was derived by well-known[1] and tested[23] conformational arguments. Thus, we have prepared the two isomers of the [Co(−)-(stien)$_3$]$^{3+}$ ion; their circular dichroism and absorption spectra are shown in Figure 5, where, in addition, we show the calculated[3] conformational and vicinal effect. The circular dichroism spectra show small intensity variations in water and dimethyl sulfoxide, but the essential shape of the curves remains the same in all solvents as it does in the solid state. The major bands of the two isomers are assigned to the $^1A_1 \rightarrow {}^1E$ transition, and the smaller negative band at higher energies observed for the (+) isomer is assigned to the $^1A_1 \rightarrow {}^1A_2$ component of the $^1A_{1g} \rightarrow {}^1T_{1g}$ manifold. We have no firm evidence for these assignments except to note first that in methanol the addition of chloride ions causes larger changes in the $^1A_2$ band than in the major band (the ion pair "criterion")[24] and second that the assignments are consistent with those established for the [Co(en)$_3$]$^{3+}$ ion.[25] If these assignments are correct, and if it is assumed that the same signs of the ^1E band will obtain for these complexes as those observed for other five-membered ring tris(diamine)cobalt complexes[26] of known absolute configuration, the isomer with the positive ^1E band has the Λ absolute configuration and that with the negative ^1E band and the Δ absolute configuration. Both complexes were equilibrated with activated charcoal, and the equilibrium circular dichroism was the same, starting from either isomer, as that of the (−) complex (*i.e.*, Δ) within 10%. The equilibration process is accompanied by some decomposition, and we were unable to obtain an accurate value of the equilibrium distribution, but there is no doubt that the isomer with the negative ^1E band predominates to the extent of at least 90% over the isomer with the positive ^1E band at equilibrium. It therefore follows[1] that the Δ-(−)-[Co(−)-(stien)$_3$]$^{3+}$ ion has its rings disposed in the *lel* orientation, that the rings have the λ conformation, and that (−)-stien has the *R*,*R* configuration. This conclusion is opposite to the one drawn previously,[27] and although our conclusion is drawn from more generally acceptable evidence, we remain reserved about the assignment we have made. In part the reason for this is that, as we shall show here and elsewhere, complexes of active stilbenediamine with our absolute assignment give circular dichroism spectra which are inverted to those formed with corresponding diamines with established configurations.

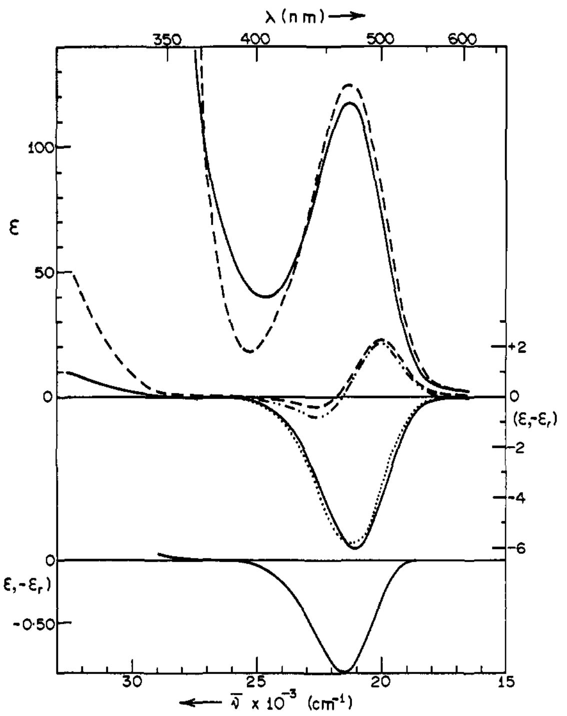

Figure 5. The absorption and circular dichroism spectra of the (+)-[Co (−)stien$_3$]$^{3+}$ (---) and the (−)-[Co (−)stien$_3$]$^{3+}$ (—) ions in methanol solutions. The two curves (-· ·-) and (· · · ·) are measured in a 100-fold excess of Cl$^-$ ions and the lower circular dichroism curve is the calculated "vicinal" contribution.

The absolute configuration of the *trans*-*S*,*S*-[Co-2,3,2-tetCl$_2$]$^+$ ion was assigned also on the basis of conformational arguments. The reaction of 1,3-dibromopropane with excess *R*pn leads to an isomeric mixture of quadridentate ligands with the 2,3,2-tet skeleton but with *R* chiral centers on the terminal arms. We have not separated the amines, but the *trans*-dichloro–cobalt(III) complex isolated from a charcoal-equilibrated reaction between the amines and cobalt chloride has a circular dichroism spectrum which is almost identical with that which we describe here for the *trans*-*S*,*S*-[Co-

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(16) A. Nakahara, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Jap.*, **25**, 331 (1952).

(17) F. Marumo, Y. Utsumi, and Y. Saito, *Acta Crystallogr., Sect. B*, **26**, 1492 (1970).

(18) J. W. Turley and R. G. Asperger, *Inorg. Chem.*, **10**, 558 (1971).

(19) W. T. Robinson, D. A. Buckingham, G. Chandler, L. G. Marzilli, and A. M. Sargeson, *Chem. Commun.*, 539 (1969).

(20) F. H. Dickey, W. Fickett, and H. J. Lucas, *J. Amer. Chem. Soc.*, **74**, 950 (1952).

(21) D. A. Buckingham, P. A. Marzilli, A. M. Sargeson, S. F. Mason, and P. B. Beddoe, *Chem. Commun.*, 433 (1967).

(22) F. Mizukami, H. Ito, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jap.*, **43**, 3633, 3973 (1970).

(23) A. M. Sargeson, "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N. Y., 1964, Chapter 5.

(24) S. F. Mason and B. J. Norman, *Proc. Chem. Soc., London*, 339 (1964); *Chem. Commun.*, 13 (1965).

(25) A. J. McCaffery and S. F. Mason, *Mol. Phys.*, **6**, 359 (1963).

(26) R. E. Ballard, A. J. McCaffery, and S. F. Mason, *J. Chem. Soc.*, 2883 (1965).

(27) R. D. Gillard, *Tetrahedron*, **21**, 503 (1965).

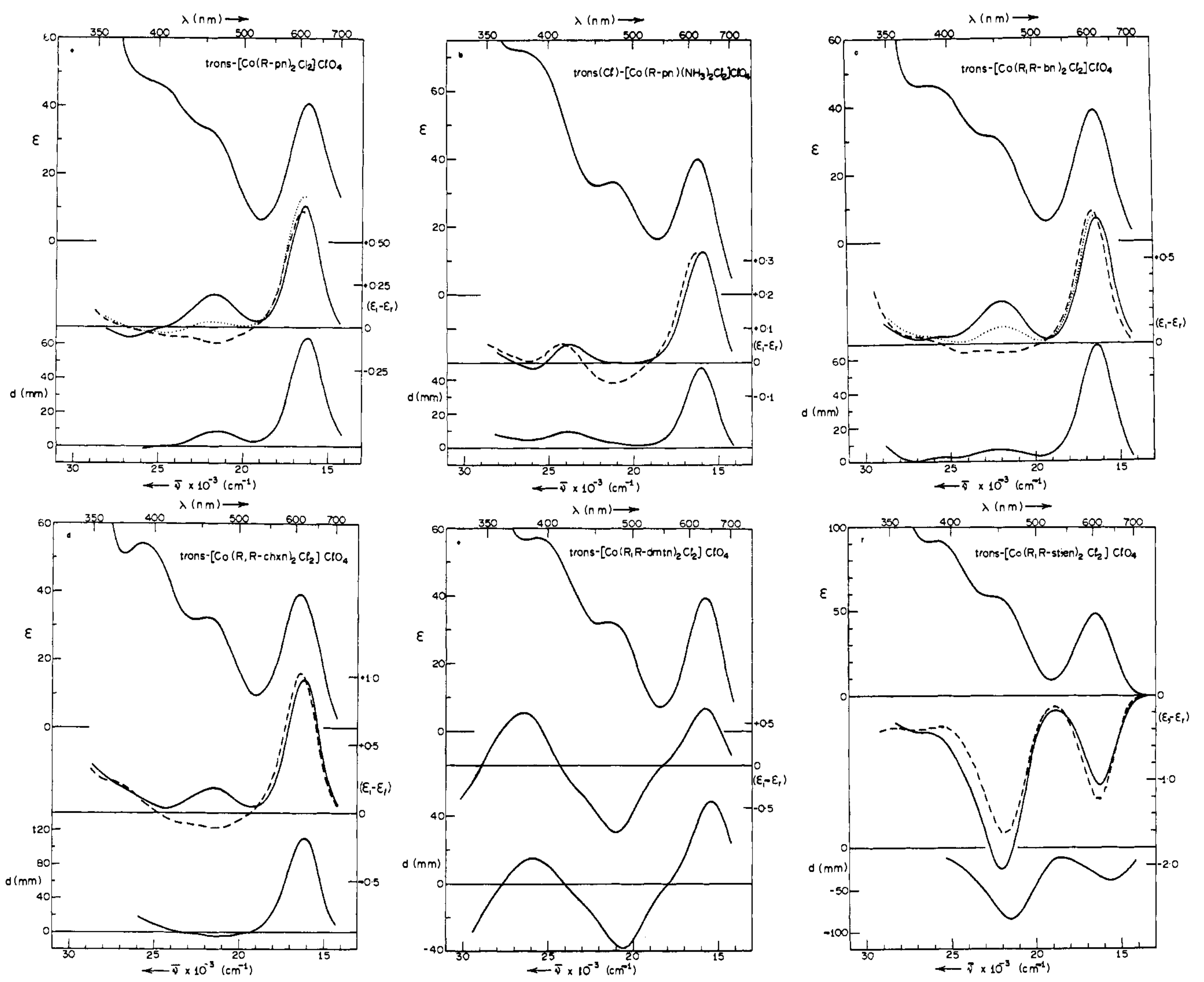

Figure 6. The circular dichroism spectra of the diamine–cobalt(III) complexes. The 1% KBr disk spectra, recorded at a sensitivity of 5 mdeg cm^{-1}, are shown at the bottom of each diagram; the dimethyl sulfoxide solution spectra (—), the dimethylformamide spectra (····), and the methanol solution spectra (-----) are also shown. All the absorption spectra are recorded in methanol, except for that of *trans*-[Co*R*-(pn)$_2$Cl$_2$]$^+$, which is in dimethyl sulfoxide. The circular dichroism of the dmtn system is in methanol.

2,3,2-tetCl$_2$]$^+$ ion. We therefore conclude that the two spectra refer to the same absolute configuration of the three chelate rings. In the methyl-substituted derivatives, the terminal arms of the ligand will be in the λ conformation for the stable equatorial disposition of the methyl groups irrespective of the isomer of the quadridentate ligand. The equatorial demands of the methyl groups then fix the absolute configuration of the total complex in the *S*,*S* absolute configuration. This assignment is the configuration that would be deduced from the previously[28] suggested absolute configuration of the chemically related *cis*-β-[Co-2,3,2-tet(ox)]$^+$ ion.

All the complexes are green in color and display absorption spectra which are characteristic of the *trans*-[Co(N)$_4$(Cl)$_2$]$^+$ chromophore. We assume that all the complexes have a totally or predominantly equatorial disposition of the substituent groups. If this is so, all the five-membered ring systems, with *R* chiral centers, are in the λ conformation as are the rings in the *trans*,*trans*-*S*,*S*-[Co(*N*-Meen)$_2$Cl$_2$]$^+$ ion. The *R*,*R*dmtn is assumed to be in the λ-skew[29] conformation on the premise that the most stable ring will be the one with equatorial methyl groups. The *trans*-*R*,*R*-[Co(trien)-Cl$_2$]$^+$ ion has the two terminal chelate rings in the λ conformation, while the central ring is in the δ conformation. Similarly the *trans*-*S*,*S*-[Co-2,3,2-tetCl$_2$]$^+$ ion has the conformations λ, δ-skew, λ for the ring sequence.

(5) Results

It is usually assumed that a molecule shows optical activity which is largely or solely determined by its molecular framework and is not greatly affected by its surroundings—the dilute hypothetical gas. Such an assumption is generally incorrect for the present series of complexes and we take the historically[30] important ion *trans*-[Co*R*(pn)$_2$Cl$_2$]$^+$ as the first example which reveals the problem. Figure 6 shows the absorption spectrum of *trans*-[Co*R*(pn)$_2$Cl$_2$]ClO$_4$ in dimethyl sulfoxide solution and the circular dichroism spectra in

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[28] G. R. Brubaker and D. P. Schaefer, *Inorg. Chem.*, 10, 811 (1971).

[29] B. Bosnich, W. R. Kneen, and A. T. Phillip, *ibid.*, 8, 2567 (1969).

[30] J. P. Mathieu, *Ann. Phys. (Leipzig)*, 19, 335 (1944); J. H. Dunlop and R. D. Gillard, *Mol. Phys.*, 7, 493 (1964); R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, 4, 202 (1965); C. J. Hawkins, E. Larsen, and I. Olsen, *Acta Chem. Scand.*, 19, 1915 (1965).

methanol, dimethyl sulfoxide, dimethylformamide, and in a 1% KBr disk. The absorption spectrum for the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition is essentially the same for all solvents, and the circular dichroism in any given solvent does not vary appreciably with the concentration or the addition of Cl^- and ClO_4^- ions. This latter observation suggests that ion pairing does not have a drastic effect on the circular dichroism and that the changes observed are due to the solvent. The band at around 16,000 cm^{-1} is the $^1A_{1g} \rightarrow {}^1E_g$ transition, while the band at 21,500 cm^{-1} is the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition,[31] both of which are derived from the $^1A_{1g} \rightarrow {}^1T_{1g}$ manifold. It will be seen that whereas the circular dichroism of the $^1A_{1g} \rightarrow {}^1E_g$ transition does not vary appreciably with changes in solvent, that of the $^1A_{1g} \rightarrow {}^1A_{2g}$ excitation is relatively weak and changes sign according to the solvent. It seems certain that the solvent molecules are dissymmetrically solvating the ion to cause these changes in the $^1A_{2g}$ band. These solvation effects may induce the changes by the solvent molecules orienting themselves about the complex in a dissymmetric array at similar distances as the coordinated groups and by causing dissymmetric distortions of the donor atoms. It is not difficult to postulate hydrogen-bonded solvent structures about the dissymmetric ion which will meet these demands, but in the absence of any firm evidence we prefer not to speculate on the possible structures. Our main concern is to find a spectrum which is devoid of these environmental complications. It is for this reason that we have resorted to the KBr disk technique.

The solid KBr disk spectrum shows that both the $^1A_{2g}$ and ^1E_g bands are positive, although the former is very much weaker. We have found that the Cl·HCl salt, the tetraphenylboron, the Cl^-, and the shown ClO_4^- salts all give essentially the same solid circular dichroism spectra, except that there are small changes in relative intensity but not a change in sign. This is generally true for all of the present series of complexes where we have changed the counterion. It should be pointed out, however, that we have found other complexes, which we will describe elsewhere, that sometimes do show large changes in intensity with change in anion. This is generally observed when perchlorates are compared to halides, and we suspect that in some way this is related to the high thermal disorder usually found in perchlorate crystal structures. The fact that the solid-state circular dichroism of the present series of complexes is largely insensitive to the nature of the anion does not solve the problem of finding the hypothetical gas spectrum since, in the crystal, any given molecule is surrounded by its dissymmetric neighbors which, by their influence on each other, can engender mutual dissymmetric perturbations. Further, structures are known where molecules in the same unit cell have different distortions of their molecular frameworks,[18] and presumably similar differences will occur when the counterion is changed. In order to ascertain the order of magnitude of these effects, we have measured the solid-state circular dichroism of a series of symmetrical cobalt(III) complex cations precipitated with optically active counteranions.[5] It was observed that in all cases the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition components showed optical activity but it was always an order of magnitude less than that shown by the conformational optical activity of the ^1E_g band of the present series of complexes, although it is of comparable magnitude to that observed for the $^1A_{2g}$ transition in some of the substituted diamine complexes. Since the solid-state spectra appear to give the most reliable measure of the true hypothetical gas circular dichroism, we shall use these here for our interpretation although it is recognized that, for weak bands ($\epsilon_l - \epsilon_r \gtrsim 0.2$), the effects of crystal forces may lead to ambiguity.

We now consider the circular dichroism spectra of the mono- and bisalkyl-substituted diamine complexes, the spectra of which are shown in Figure 6. Leaving aside the *trans*-[Co*R*,*R*(stien)$_2$Cl$_2$]$^+$ ion with its inverted circular dichroism for the present, we note that in all cases the ^1E_g band is positive, and changes in solvent cause changes which appear to be small. These observations do not necessarily imply that both components of the ^1E_g band are of the same sign, since the bands may consist of a major positive component which dominates a smaller negative one. It is not difficult to analytically reproduce most of these ^1E_g bands in these terms, but we have no evidence to justify such a procedure. It will be seen that the ^1E_g band intensity for the *trans*-(Cl$_2$)-[Co*R*pn(NH$_3$)$_2$Cl$_2$]$^+$ ion (which is the same as that of [Co*R*pn(NH$_3$)$_4$]$^{3+}$) is roughly half that of the *trans*-[Co*R*(pn)$_2$Cl$_2$]$^+$ ion, implying that the contributions from the rings are additive. Further, for the five-membered ring bidentate complexes, the intensity of the ^1E_g band is roughly the same irrespective of the nature or number of the substituents on the alkyl groups of the ring; the variation is at most 20%. This suggests, as might be expected from the sharp variation of the O_h potential with distance, that the vicinal effect is a small contributor to the optical activity. However, ring substituents may cause differing distortions of the donor atoms and it is difficult, without crystallographic evidence, to be certain of the precise origins of the vicinal effect except to note that it is small.

The $^1A_{2g}$ band presents quite a different problem, and it will be seen that, in the solid, we have obtained all possible combinations of sign. Thus the $^1A_{2g}$ band is positive for *trans*-[Co*R*(pn)$_2$Cl$_2$]$^+$, negative for *trans*-[Co*R*,*R*(chxn)$_2$Cl$_2$]$^+$, and practically zero for *trans*-(Cl$_2$)-[Co*R*pn(NH$_3$)$_2$Cl$_2$]$^+$. This apparently haphazard behavior leads us to postulate that the sign of the $^1A_{2g}$ band and also that of the ^1E_g band is determined by the opposing contributions of the alkyl groups of the rings and the dissymmetric distortions of the donor atoms. Assuming that all the five-membered ring systems have the same chirality of donor atom distortions as that observed for the *trans*-[Co*R*(pn)$_2$Cl$_2$]$^+$ ion, and that both the alkyl and donor groups have a net repulsive potential, we attempt the following explanation of the results.

Considering the *trans*-[Co*R*(pn)$_2$Cl$_2$]$^+$ ion first, we note that for its λ-conformation of the rings, the alkyl groups span positive sectors and the donor atoms lie largely in negative sectors of the (repulsive) potential, and it appears that the alkyl group perturbation is more important for both the $^1A_{2g}$ and ^1E_g bands.

Although there are more rigorous and sophisticated discussions that can be given, we assume that the com-

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[31] S. Yamada, A. Nakahara, Y. Shimura, and R. Tsuchida, *Bull. Chem. Soc. Jap.*, 28, 222 (1955); C. J. Ballhausen and W. Moffitt, *J. Inorg. Nucl. Chem.*, 3, 178 (1956); R. Dingle, *J. Chem. Phys.*, 46, 1 (1967).

ponents of the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition essentially involve the following one-electron excitations: $d_{xy} \rightarrow d_{x^2-y^2}$ [($^1B_1(D_2)$), ($^1A_{2g}(D_{4h})$)], $d_{xz+yz} \rightarrow d_{x^2-y^2}$ ($^1B_2(D_2)$) and $d_{xz-yz} \rightarrow d_{x^2-y^2}$ ($^1B_3(D_2)$). The $d_{x^2-y^2}$ orbital is common to all three components, and in any comparison of the three components we need consider only the other three orbitals, although the circular dichroism will be determined by the perturbation of all the dissymmetric atoms and groups on all the relevant orbitals. It will be evident that the d_{xy} orbital is more closely aligned to the (distorted) donor atoms than the other two orbitals, and we would expect that, for *trans*-[CoN$_4$Cl$_2$]$^+$ complex ions, the $^1A_{2g}$ circular dichroism band would be more sensitive to donor atom distortions than the other two. In addition, because the d_{xz-yz} orbital points almost directly at the alkyl groups, we would anticipate that the sign of the transition involving this orbital would be affected more by the alkyl groups. The other ^1E_g component orbital, d_{xz+yz}, points at right angles to d_{xz-yz} and we would expect that it would be affected most by the amino hydrogen atoms at which it is most closely directed. The amino hydrogen atoms lie in negative sectors of the repulsive potential. We suspect, however, that these hydrogen atoms represent an attractive potential for the d electrons. The reason for this assumption is based on the observation that these hydrogen atoms are acidic in many complexes, which may imply that the N–H bond is very polar owing to a strong displacement of electrons toward the nitrogen atom. This will then leave a highly deshielded nucleus which may have a net attractive effect on the d electrons. The result would be that both the amino hydrogen atoms and the alkyl groups would contribute to give the same (positive) sign of the circular dichroism. Thus, if the $d_{xz-yz} \rightarrow d_{x^2-y^2}$ transition is affected most by the alkyl groups and the $d_{xz+yz} \rightarrow d_{x^2-y^2}$ transition is affected most by the amino hydrogen atoms, both components of the ^1E_g band should give positive circular dichroism for the λ ring conformation and both will not be affected as much as the $^1A_{2g}$ band by donor atom distortions. We assume that the weakness of the $^1A_{2g}$ band compared with the ^1E_g band is because of the more effective donor atom distortion effect opposing the alkyl group contribution in the former. This assumption is consistent with the observations that all five-membered ring systems (except *trans*-[Co*R*,*R*(stien)$_2$Cl$_2$]$^+$) show a strong positive ^1E_g band and a weak $^1A_{2g}$ band of varying sign. Thus we suppose that for the *trans*-[Co*R*(pn)$_2$Cl$_2$]$^+$ and *trans*-[Co*R*,*R*(bn)$_2$Cl$_2$]$^+$ ions, which both have positive $^1A_{2g}$ bands, the alkyl groups are more important than the donor atom distortions in determining the sign of the circular dichroism of this band, whereas the reverse is the case for the *trans*-[Co*R*,*R*(chxn)$_2$Cl$_2$]$^+$ ion which shows a negative $^1A_{2g}$ band. For the *trans*-(Cl$_2$)-[Co*R*pn(NH$_3$)$_2$Cl$_2$]$^+$ ion, where the $^1A_{2g}$ band is practically zero, the two effects cancel each other. These variations presumably reflect the differences which arise from substitution of the ethylenediamine system and perhaps the effects of crystal packing.

If we accept the *R*,*R* assignment for the (−)-stien ligand, the inverted spectrum observed for the *trans*-[Co*R*,*R*(stien)$_2$Cl$_2$]$^+$ ion can only be explained by the assumption that the phenyl groups and the effects they may engender in distorting the system dominate in contributing to the optical activity and that these effects are opposed in sign to saturated alkyl groups.

The remaining complex ion *trans*-[Co*R*,*R*(dmtn)$_2$Cl$_2$]$^+$ is assumed to have its rings in the λ-skew conformation. The central carbon atom of this ring will lie at the intersection of two nodal planes, while the two hydrogen atoms attached to it will encompass negative sectors. The other alkyl groups will lie largely in positive sectors. Presumably, the donor nitrogen atoms will be skewed as in the *trans*-[Co*R*(pn)$_2$Cl$_2$]$^+$ ion, but we are unaware of any crystallographic evidence which indicates the N–Co–N bond angle and the degree of twist of the donor atoms in a free perfectly skewed six-membered ring. The sector occupation of the donor groups depends critically on the N–Co–N angle and the degree of twist of the donor atoms. If we assume the assigned absolute configuration and that the nitrogen atoms lie in sectors of opposed sign to the alkyl groups, then we may offer an explanation for the observed circular dichroism similar to that for the five-membered ring systems. It is perhaps worth pointing out that in a skew ring the equatorial amino hydrogen atoms lie in opposing sectors to the alkyl groups, while the axial amino hydrogen atoms are close to a nodal plane but probably in sectors of the same sign as the alkyl groups. In addition, because the six-membered ring is larger than the five-membered system, the hydrogen atoms attached to the 1,3 carbon atoms tend to lie more in opposing sectors than they do when attached to the corresponding carbon atoms in the five-membered ring systems.

Our assumptions concerning the different perturbations experienced by the various orbitals due to their different orientations are to some extent reinforced when the spectra shown by the *trans*,*trans*-*S*,*S*-[Co(*N*-Meen)$_2$Cl$_2$]$^+$, *trans*-*R*,*R*-[Co-2,3,2-tetCl$_2$]$^+$, and *trans*-*R*,*R*-[Co(trien)Cl$_2$]$^+$ ions are considered. These are shown in Figure 7, where we note that the *trans*-*R*,*R*-[Co(trien)Cl$_2$]$^+$ ion shows a strong solvent effect for its $^1A_{2g}$ band and, more significantly, all the ^1E_g bands of the three ions are split into a positive and negative component. There seems little doubt that the ^1E_g band of the *trans*,*trans*-*S*,*S*-[Co(*N*-Meen)$_2$Cl$_2$]$^+$ ion consists of positive and negative components, where the positive band, represented by the saddle at about 17,000 cm^{-1}, is overwhelmed by the stronger negative band.[32] In the corresponding *N*-methyl-*R*-propylenediamine complexes[33] the ^1E_g band consists of two clearly defined positive and negative peaks in positions which would support the interpretation of the ^1E_g band for the *N*-methylethylenediamine system.

We first consider the *trans*-*R*,*R*-[Co(trien)Cl$_2$]$^+$ ion which has the λ, δ, λ sequence of its rings. The orbitals involved in the $d_{xy} \rightarrow d_{x^2-y^2}$ transition are equally disposed to the three rings, which implies that the three rings will contribute roughly equally to the circular dichroism of this band. But since two of the rings are λ and one is δ, the average perturbation will be roughly equal to a single λ ring if we ignore the differing distortions of the donor atoms of the three rings. Thus, if the perturbation of the alkyl groups is the most important effect, the $^1A_{2g}$ band should be positive, as is observed. For the case of the ^1E_g band, the lobes of

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[32] D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, 7, 915 (1968).

[33] M. Saburi, Y. Tsujito, and S. Yoshikawa, *ibid.*, 9, 1476 (1970).

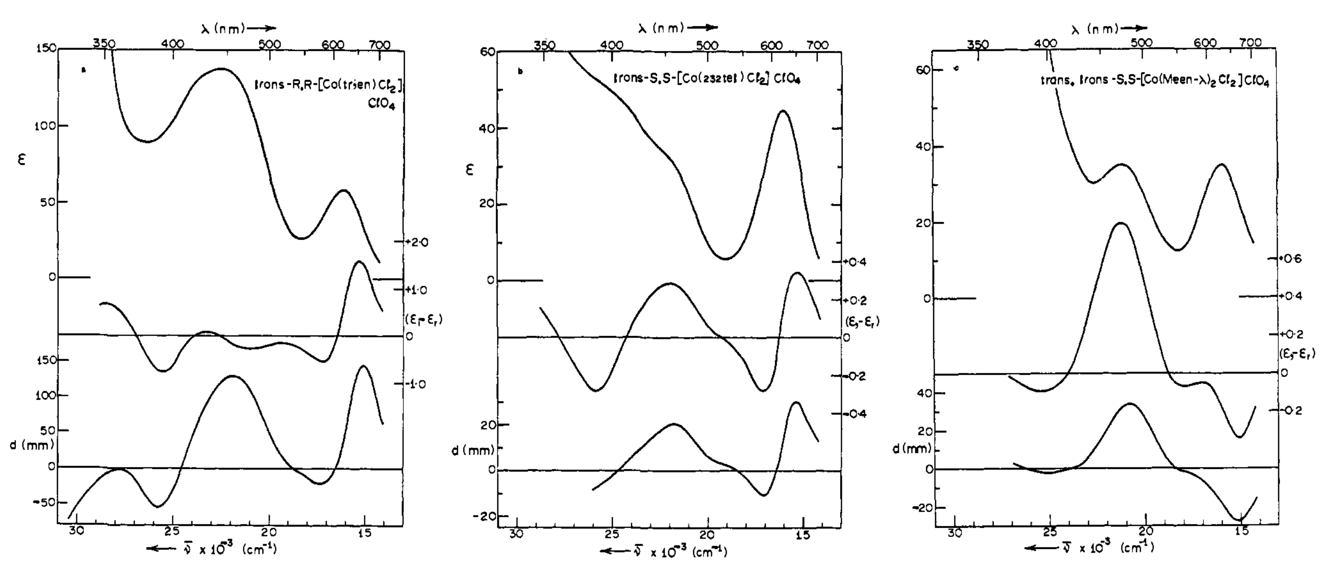

Figure 7. The quadridentate amine- and substituted bis(diamine)–cobalt(III) complex absorption and circular dichroism spectra in dimethylformamide solution. The lower curves are the KBr disk spectra.

the d_{xz+yz} orbital involved in the transition $d_{xz+yz} \rightarrow d_{x^2-y^2}$ point mainly at the two terminal λ rings, whereas the d_{xz-yz} orbital of the $d_{xz-yz} \rightarrow d_{x^2-y^2}$ transition points mainly at the inner δ ring and the terminal hydrogen atoms which, although they lie in opposing sectors to the CH_2 groups, will contribute the same sign as the CH_2 groups if the amino hydrogen atoms are assumed to represent an attractive potential. If the major perturbation to the $d_{xz+yz} \rightarrow d_{x^2-y^2}$ transition is due to the two λ rings and the $d_{xz-yz} \rightarrow d_{x^2-y^2}$ excitation is perturbed mainly by the δ ring and the terminal hydrogen atoms, we would expect the former component to engender positive circular dichroism while the latter should impart negative circular dichroism to the respective transitions. This pattern is observed. Of course both orbitals will be perturbed by all three rings, but we assume that the plus–minus pattern of the ^1E_g band is due to the differences in orientation of the orbitals with respect to the rings. Furthermore, because all three rings perturb all the orbitals to varying degrees, we need not necessarily expect, as we observe here, that a plus–minus pattern of the ^1E_g band will be observed in all complexes where the rings are of mixed chirality since, although the argument is partly based on symmetry, it also involves considerations of the relative magnitudes of all sources of perturbation.

We may interpret the circular dichroism of the *trans*-*S*,*S*-[Co-2,3,2-tetCl$_2$]$^+$ ion in a similar way if we assume that a six-membered ring contributes roughly the same amount to the optical activity as the five-membered rings. That this is probably so is seen in the spectrum of the *trans*-[Co*R*,*R*(dmtn)$_2$Cl$_2$]$^+$ ion, for which the ^1E_g band carries roughly the same rotational strength as the ^1E_g bands of the bisdiamine systems with five-membered rings. Thus the sign of the $^1A_{2g}$ band will be determined by the average contributions of the λ, δ-skew, λ rings of the *trans*-*S*,*S*-[Co-2,3,2-tetCl$_2$]$^+$ ion to the symmetrically oriented orbitals of the $d_{xy} \rightarrow d_{x^2-y^2}$ excitation, which would lead to the observed net positive contribution to the $^1A_{2g}$ band. The lobes of the d_{xz+yz} orbital point mainly at the two terminal λ rings, while those of the d_{xz-yz} orbital point mainly at the inner δ-skew ring, and we may expect, as is observed, that one component of the ^1E_g band will be positive and the other negative. Molecular models indicate that the pairs of terminal amino-hydrogen atoms of this complex lie in sectors of opposed sign, and we expect that the effect of these four protons would lead to almost total cancellation. This observation and the fact that this and the *trans*-*R*,*R*-[Co(trien)Cl$_2$]$^+$ ion show very similar circular dichroism suggests, as we have asserted earlier, that the amino hydrogen atoms do not seem to have a dominating effect on the circular dichroism of these systems. We are uncertain of the sector occupancy of the two inner amino hydrogen atoms in either of these two quadridentate systems, since small distortions may cause displacements to opposing sectors.

The *trans*,*trans*-*S*,*S*-[Co(*N*-Meen)$_2$Cl$_2$]$^+$ ion has two sources of perturbation superimposed on the D_{4h} perturbation. The first is a D_{2h} perturbation due to the fact that the donor nitrogen atoms are inequivalent and the second, a D_2 perturbation, due to the donor atom distortions and to a lesser extent the effect of the alkyl groups. This will rotate the axis frame of quantization to lie somewhere between the *x*, *y* axes and the *x′*, *y′* axes (Figure 4). If we assume, however, that the quantization is nearly the same as that appropriate for D_2 symmetry (Figure 4), we may interpret the circular dichroism as follows. The CH_2 groups of the ethylenediamine rings lie in positive sectors, while the two (equatorial) methyl groups lie close to a node but mainly in negative sectors. We assume that the perturbation of a methyl group is roughly equivalent to a CH_2 group for equivalent dispositions in a given sector; then the average perturbation experienced by the orbitals of the $d_{xy} \rightarrow d_{x^2-y^2}$ transition is roughly equivalent to a λ ring and therefore the $^1A_{2g}$ band should be positive as is observed. The $d_{xz+yz} \rightarrow d_{x^2-y^2}$ transition is perturbed more by the methyl groups and the amino hydrogen atoms than it is by the CH_2 groups, and therefore this transition should give negative circular dichroism. Because the $d_{xz-yz} \rightarrow d_{x^2-y^2}$ transition is perturbed more by the CH_2 groups, it should give positive circular dichroism. Although a plus–minus pattern is observed under the ^1E_g band in this case, it is readily apparent that if the positive com-

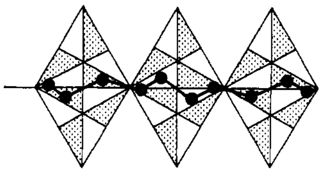

Figure 8. The assumed atomic positions of the carbon and nitrogen atoms in the *trans-R,R*-[Co(trien)Cl$_2$]$^+$ ion and their sector occupancy in the simplest O_h pseudoscalar potential. A plane view of the potential is shown.

ponent were a little weaker or the negative component stronger or both, or that the components were not as well separated, the ^1E_g band would give the appearance of a single negative band. This emphasizes our earlier point that both the magnitude of the perturbation to and the orientations of the orbitals have to be considered in rationalizing the behavior of the components of the ^1E_g band.

The foregoing discussion of the ^1E_g band assigned the two components in a way which was consistent with our assumption about the nature of the perturbation of the orbitals involved in the respective transitions. We have no independent evidence for the assignments of the components. Furthermore, we have assumed in the last three cases that the major perturbing effect was due to the alkyl groups, and we have assumed the contributions from the donor atom distortions are less important. Based on the determined[18] distortions of the donor atoms of a similar compound to *trans*-[Co(trien)Cl$_2$]ClO$_4$, we anticipate that the trien system will have the donor atom distortions depicted in Figure 8. It will be noted that the two terminal nitrogen atoms lie mainly in negative sectors, whereas the two inner ones lie mainly in positive sectors. While retaining the same sign of the potential, it may be possible to rationalize the plus–minus pattern of the ^1E_g band of the *trans*-[Co(trien)Cl$_2$]$^+$ ion in terms which assume the donor atom distortions to have the most important perturbation. Since the nitrogen atoms lie in opposing sectors to the CH$_2$ groups, the result of donor atom perturbation may lead to a reversal of the assignments made for the ^1E_g band. There are, however, difficulties in rationalizing the sign of the $^1A_{2g}$ band in these terms, although, as we shall show elsewhere, certain quadridentate ligand octahedral complexes show circular dichroism which appears to be dominated by the donor atom distortion effect.

We should allude briefly to the relative magnitudes of the rotational strengths for this series of complexes. Thus, on a simple basis we might have expected the $^1A_{2g}$ bands of the *trans,trans-S,S*-[Co(*N*-Meen)$_2$Cl$_2$]$^+$ and *trans*-(Cl$_2$)-[Co*R*pn(NH$_3$)$_2$Cl$_2$]$^+$ ions to show comparable intensities since, roughly, both reflect the contributions of a single λ ring. The fact that the two are quite different in intensity perhaps is due to differences in donor atom distortions in the two cases.

Finally, we point out that for point groups of lower symmetry than D_2 the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition can mix with at least one of the states of the $^1A_{1g} \rightarrow {}^1E_g$ transition. Depending on the extent of mixing, the nature of the resultant states may lead to problems in interpreting the sign patterns under the $^1T_{1g}$ manifold. We have ignored this effect as we have ignored mixing with the $^1T_{2g}$ states, although, in some cases, the circular dichroism under the $^1T_{2g}$ manifold is as large as that observed under the $^1A_{1g} \rightarrow {}^1T_{1g}$ transitions. The strongest circular dichroism under the $^1A_{1g} \rightarrow {}^1T_{2g}$ transition appears in complexes, such as the *trans*-[Co(trien)Cl$_2$]$^+$ ion, which we suspect may have large donor atom distortions. To have included complete mixing within the d-electron manifold, and the necessary mixing of higher states of odd parity, would have divested the foregoing presentation of any ready applicability.

(6) Discussion

The present theory is consistent with the conformational circular dichroism spectra observed in solution for all recorded polyamine complexes[18,31,34,35] with axially symmetrical unidentate ligands except for two quadridentate[18,35] cases where the $^1A_{2g}$ band is reversed in sign. We expect, however, that the $^1A_{2g}$ bands in these complexes will reverse in sign in the solid as we have observed for the *trans-R,R*-[Co(trien)Cl$_2$]ClO$_4$ complex. For systems with nonaxially symmetrical groups, inversions of the circular dichroism occur compared to, for example, the *trans*-dichloro systems. Thus we have checked the circular dichroism spectra of the two complex ions *trans,trans-S,S*-[Co(*N*-Meen)$_2$(NO$_2$)$_2$]$^+$ and (the isomeric mixture) *trans,trans-S,S*-[Co(*N*-Meen)$_2$NO$_2$Cl]$^+$, and we find the solid circular dichroism very similar to that found in solution,[32] where the $^1A_{2g}$ bands are reversed in sign compared with the dichloro analog. This effect may be related to the particular orientations of the nitro groups which, in certain dispositions of the oxygen atoms in sectors of the potential, may have the effect of reversing the sign. The fact that the ^1E_g bands in these complexes do not show a plus–minus pattern is not inconsistent with the present theory, since the circular dichroism is broad and the levels are closely spaced in energy, making the observation of weaker oppositely signed components difficult. Both these questions will be discussed more fully elsewhere.

Octahedral amino acid complexes, specifically of the type [Co(NH$_3$)$_4$(amino acid)]$^{2+}$, show rather complicated circular dichroism spectra in solution. We have not investigated these and we do not know whether sign differences occur in the solid state, but we wish to make the following observation. Amino acid chelate rings[36] are very slightly puckered compared to saturated systems, but the donor atom distortions are roughly the same as the diamine systems. If our suggestion that the circular dichroism of the present series of complexes is to a large extent canceled by the opposing effects of donor atom distortions and the puckered alkyl groups is correct, it may well be that, for five-membered ring amino acid complexes which are unsubstituted at the nitrogen atom, and assuming the oxygen and nitrogen atoms have the same sign of potential, the circular dichroism is largely determined by donor atom distortions. Whatever the case, the present theory can accommodate these octahedral

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(34) M. Goto, A. Okubo, T. Sawai, and S. Yoshikawa, *Inorg. Chem.*, 9, 1488 (1970).

(35) S. Yoshikawa, T. Sekihara, and M. Goto, *ibid.*, 6, 169 (1967); M. Goto, M. Saburi, and S. Yoshikawa, *ibid.*, 8, 358 (1969).

(36) H. C. Freeman, *Advan. Protein Chem.*, 22, 257 (1967).

complexes, although due care should be taken in defining the quantization if the signs of the circular dichroism of these amino acid complexes are compared with those of the *trans*-di-X–polyamine systems.

We now return to the main object of this paper, which was to explore the possibility of enunciating a general regional rule for the optical activity of conformational isomers. With the evidence we have, we believe that a rational description of the observations has been given in terms of a general rule, but because of the number of uncertainties involved in its application it is of little practical value at the present time. In order to apply the rule we would require the following: (a) a certain knowledge that at least an approximate hypothetical gas spectrum can be obtained for these complexes, (b) some reliable predictive method of knowing the extent and direction of donor atom distortions and possibly also alkyl group conformational distortions, and (c) a knowledge of the signs and magnitudes of interaction of the various groups that contribute to the optical activity. This last piece of information is particularly critical, since we could have considered all the present data and interpreted it in an almost equally consistent way by assuming for all cases *both* the alkyl groups and the donor nitrogen atoms represented an attractive potential and that the donor atom distortions dominated the dissymmetric perturbation. Our assumption that the saturated alkyl groups and the donor atoms both had repulsive potentials was somewhat arbitrary and probably contrary to most of the current views on the subject[9] except that, in our interpretation, it avoided making a number of further assumptions about the magnitudes of various distortions of the donor atoms. For example, if we had assumed that the sign of the $^1A_{2g}$ band of the *trans*-*R*,*R*-[Co(trien)Cl$_2$]$^+$ ion was determined mainly by the "down-up-down-up" dissymmetric array of the donor nitrogen atoms, we would have been forced to make an assumption about the relative magnitudes of the contributions from the two terminal nitrogen atoms and those of the inner ones.

Finally, we allude briefly to two previous rules which have been put forward. The first is the empirical octant rule[37] which bears a primitive geometric resemblance to the present one but which, in essence, amounts to summing the supposed equal contributions of λ and δ rings in a complex. Additional elements of chirality are added[38] in an *ad hoc* way which is independent of the rule. The second[39] is a recent theoretically based interpretation which, although it is more restrictive than the present interpretation, puts forward essentially the same space delineation for certain classes of compounds. However, both ignore the effect of donor atom distortions and the contributions of amino hydrogen atoms, and both are restricted to the sign (in solution) of the $^1A_{2g}$ band or its equivalent while largely ignoring the other components of the $^1T_{1g}$ manifold, and the latter puts forward different potentials for different octahedral metal complexes which owe their optical activity only to conformational dissymmetry.

(7) Experimental Section

Preparation of Disks and the Recording of Spectra. Conformational isomers usually display circular dichroism which is weaker than that shown by configurational isomers, and some care is needed in obtaining accurate spectra in KBr disks. We have found the following method satisfactory. Dry KBr (0.2 g) and the required amount of complex were powdered in a dental amalgam mill (WIG-L-BUG, Cresent Manufacturing Co., Chicago) and 0.1 g of the powder was pressed in a standard KBr press at 10 tons/in.^{2} for 3 min. The disks prepared in this way are clear and homogeneous and have an average thickness of 0.32 ± 0.02 mm. The disk was then mounted either on the face of a spectrophotometer cell or a KBr disk holder and placed normal to the light beam. Even with apparently translucent disks, there is a large amount of depolarization of the light beam, and this seems to increase with the inhomogeneity of the disk, its "cloudiness," the intensity of the absorption band under investigation, and the concentration of the sample in the KBr. We have found that, for a given band, there exists a linear relationship between the circular dichroism deflection and the sample concentration between 0 and 5% of sample; thereafter, circular dichroism can still be recorded even with 30% sample disks, but the deflection was roughly constant for disk concentrations above about 15%. Disk concentrations between 0.5 and 2% gave the most satisfactory results for these complexes. For weakly active complexes, the Roussel–Jouan Dichrographe (Mark II) was found to give at high sensitivity a nearly constant positive deflection which increased with the amount of depolarization. We have been able to observe this effect even with optically inactive samples of the compounds. The modified Durrum-Jasco SS-20 instrument appears to be devoid of this characteristic, and the solid spectra recorded here were measured with this instrument. Since the intensities of all the normal absorption bands in the region between about 370 and 700 nm are about the same, the relative intensities of all the circular dichroism deflections in this region are probably accurate for a given complex. In no case was there any evidence to suggest that bromide substitution had occurred during or subsequent to the disk preparation.

The solution circular dichroism spectra were measured with a Roussel-Jouan (Mark II) Dichrographe except between 610 and 700 nm, where the Durrum-Jasco instrument was used. The linear absorption spectra were recorded with a Unicam-SP800 spectrophotometer. Many of the complexes react fairly rapidly with some of the solvents to form usually cis solvento complexes. We have taken due care in selecting the solvent and checking for any complications that may arise from solvent intervention.

Preparation of *rac*- and *meso*-2,4-Diaminopentane. In order to obtain the yields recorded by Dippel[40] in his ethanol–sodium reduction of acetylacetone dioxime,[41] the conditions have to be adjusted so that molten spinning globules of sodium are generated for most of the reaction time. Large-scale preparations by this method gave the impression of imminent violence, and we sought a somewhat calmer reaction for the preparation. The following method gives the same yields of products and can be used with large quantities without hazard.

Acetylacetone dioxime (130 g) was dissolved in a cold solution of sodium hydroxide (360 g) in water (3 l.) and Raney nickel alloy (250 g) was added in small portions to this solution, which was vigorously stirred and efficiently cooled, at such a rate that the solution temperature did not rise above 30°. After the addition was complete (*ca.* 2 hr), the mixture was allowed to stand at room temperature overnight and the Raney nickel was filtered off (caution) and washed with water. The combined filtrates were steam distilled until no further amine was detected (CuCl$_2$ in ethanol). The distillate (*ca.* 3.5 l.) was neutralized with hydrochloric acid (*ca.* 150 ml, 12 *M*) and evaporated to dryness to give a somewhat hygroscopic yellow mixture of amine hydrochlorides. From this solid the amines were regenerated and distilled by Dippel's method[40] giving a colorless liquid. This was dissolved in methanol (500 ml) and cautiously neutralized with hydrochloric acid (12 *M*). After evaporation under reduced pressure, a dry white solid was obtained (110 g, 63%). This last procedure removed a material, present in the products from either reduction method, which otherwise made the *meso*-diamine dihydrochloride obtained in the subsequent separation hygroscopic.

Separation of the *rac*- and *meso*-2,4-Diaminopentane Dihydrochlorides. The racemic hydrochloride has a solubility of about 0.1 g/100 ml of boiling ethanol, whereas the meso isomer is soluble to

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(37) C. J. Hawkins and E. Larsen, *Acta Chem. Scand.*, **19**, 185 (1965).

(38) C. J. Hawkins, *Chem. Commun.*, 777 (1969).

(39) S. F. Mason, *J. Chem. Soc. A*, 667 (1971).

(40) C. J. Dippel, *Recl. Trav. Chim. Pays Bas*, **50**, 525 (1931).

(41) C. Harries and T. Haga, *Ber.*, **32**, 1191 (1893).

the extent of about 3.3 g/100 ml, and we have used this difference for the separation of the isomers.

The purified mixture of racemic and meso hydrochlorides (300 g) was stirred in boiling absolute ethanol (6 l.) for 45 min. The mixture was cooled rapidly in cold water to room temperature and, after remaining undisturbed for 30 min, the fine white crystals of the nearly pure racemic compound were filtered, washed with ethanol (500 ml) which was combined with the filtrate, and then with acetone followed by ether, the filtrates from which were discarded. The solid was dissolved in aqueous hydrochloric acid (200 ml, 1 *M*) at 80° and was precipitated with ethanol (200 ml) followed by the slow addition of acetone (1400 ml). The mixture was cooled, and after 1 hr, the clusters of fine white nonhygroscopic needles were collected and washed with acetone followed by ether to give the pure racemic hydrochloride (125 g).

The ethanol filtrate from the extraction was evaporated to dryness and the residue taken up in boiling methanol (650 ml). Ether (250 ml) was added slowly to the hot solution, and after the mixture was allowed to stand for 12 hr at 0° the large chunky colorless crystals of essentially pure meso hydrochloride were filtered and washed with methanol–ether (1:1) followed by ether. Recrystallization from boiling methanol by the addition of ether gave 72 g of the pure meso isomer.

Separation of the racemic and meso mixture that remained in the filtrate from the first methanol–ether precipitation proved difficult, as any extraction or fractional crystallization of the solid invariably provided a mixture, and the proportions appeared to be kinetically rather than thermodynamically controlled. However, by very slow fractional crystallization from methanol–ether, the meso compound could be obtained as the recognizable large, chunky crystals which were distinguishable from the attendant small, light needles of the racemic isomer. A rough mechanical separation was then possible, and by repeating such crystallizations and separations several times on the numerous fractions obtained, a further 30 g of the pure meso compound and about 5 g of the racemic isomer were obtained.

The two isomers can be distinguished by their pmr spectra in D_2O (but not in D_2O–DCl), and it appears that the two forms are produced in roughly equal proportions from either reduction method. *Anal.* Calcd for $C_5H_{16}N_2Cl_2$: C, 34.3; H, 9.2; N, 16.0; Cl, 40.6. Found (racemic): C, 34.2; H, 9.4; N, 16.1; Cl, 40.5. Found (meso): C, 34.5; H, 9.0; N, 16.0; Cl, 40.4.

Resolution of *rac*-2,4-Diaminopentane. It was claimed[42] recently that this compound could be resolved with (+)-tartaric acid. We have made several attempts to repeat this resolution under the exact conditions given and have made numerous attempts at resolution with (+)-tartaric acid under a wide range of conditions. In no case did we obtain resolution. (+)-Camphor-10-sulfonic acid gives a poor separation from ethanol, but dibenzoyl-(+)-tartaric acid under the conditions given below gives the two pure optical isomers in relatively efficient yield.

A hot filtered solution of dibenzoyl-(+)-tartaric acid monohydrate (111 g) in absolute ethanol (1 l.) was added to a solution of freshly distilled *rac*-2,4-diaminopentane (30 g) in water (200 ml). Small white crystals of the diastereoisomer began to form at once and on standing overnight at 0° these were collected and washed with ethanol followed by ether: yield 63 g, $[\alpha]_D$ −86.5° (1% in water). Recrystallization from hot water (100 ml) by the addition of absolute ethanol (500 ml) gave lustrous white flakes in almost quantitative recovery, $[\alpha]_D$ −91°. This rotation did not change with further crystallizations. *Anal.* Calcd for (the monohydrate) $C_{23}H_{30}N_2O_9$: C, 57.7; H, 6.3; N, 5.9. Found: C, 57.2; H, 7.0; N, 5.9.

To obtain the active amine hydrochloride, the recrystallized diastereoisomer was taken up in hot water (50 ml), mixed with methanol (400 ml) containing hydrochloric acid (35 ml, 12 *M*), and diluted with ether (500 ml). Long white needles soon began to form, and the precipitation was complete after the solution was allowed to stand at 0° for 12 hr, whereafter they were collected and washed successively with ethanol, acetone, and ether: yield 19.3 g, $[\alpha]_D$ +17° (1% in 1 *M* HCl). Fractional crystallization from hydrochloric acid (30 ml, 1 *M*) and ethanol (30 ml) by the successive addition of acetone gave fractions all of which had the same rotation, $[\alpha]_D$ +17°, and the material was recovered quantitatively after 200 ml of acetone was added. *Anal.* Calcd for ((+) isomer) $C_5H_{16}N_2Cl_2$: C, 34.3; H, 9.2; N, 16.0; Cl, 40.6. Found: C, 34.2; H, 9.2; N, 16.0; Cl, 40.4.

The water–ethanol filtrate from the precipitated diastereoisomer was evaporated to a syrup which was then taken up in hot water (50 ml) to which was added ethanol (400 ml) containing hydrochloric acid (35 ml, 12 *M*). Ether (500 ml) was added and the solution kept at 0° for 12 hr, giving, after filtration, 22.8 g of small white crystals, $[\alpha]_D$ −14.2° (1% in 1 *M* HCl). These were taken up in hot hydrochloric acid (40 ml, 1 *M*) diluted with ethanol (40 ml), followed by acetone (250 ml.). After standing for 12 hr at 0°, the long white crystals were collected and washed as before: yield 18.2 g, $[\alpha]_D$ −17° (1% in 1 *M* HCl). Further addition of acetone to the filtrate gave a powder which had a small negative rotation and was discarded. *Anal.* Calcd for ((−) isomer) $C_5H_{16}N_2Cl_2$: C, 34.3; H, 9.2; N, 16.0; Cl, 40.6. Found: C, 34.4; H, 9.2; N, 15.9; Cl, 40.7.

A small amount of the amine from the (+) hydrochloride was regenerated and distilled by the usual method.[40] The free amine from the (+) hydrochloride gave a rotation $[\alpha]_D$ −68° (0.8% in benzene), but a titration indicated that it was probably a monohydrate.

Preparation of the (+) and (−) Diastereoisomers of $[Co(-)\text{-}(stien)_3](ClO_4)_3$. *rac*-Stilbenediamine was prepared[43] and resolved[44] by known methods.

Cobalt acetate tetrahydrate (0.6 g) and (−)-stilbenediamine (1.6 g, $[\alpha]_D$ −108° in methanol) were dissolved in methanol (100 ml) and activated charcoal (0.1 g) was added. Air was passed through the solution for 16 hr, after which time it was filtered; hydrochloric acid (2 ml, 12 *M*) was added to the filtrate, and the solution was evaporated at 40° to about 5 ml. The solid remaining was suspended in methanol (30 ml) and water (100 ml). The orange solid was collected, washed with water (10 ml), and then successively slurried and filtered with three 15-ml portions of warm acetone. The first filtrate and the acetone washings were combined and set aside for the isolation of the other isomer. The remaining bright orange solid was nearly pure $(+)\text{-}[Co(-)\text{-}(stien)_3]^{3+}$ as the chloride salt (0.6 g). This was taken up in boiling methanol (250 ml), excess sodium perchlorate was added, and the solution was diluted with warm water (500 ml). After cooling at 0° for 5 hr, the fine yellow needles were collected, washed with water, and dried. The solid was taken up in a minimum amount of hot acetone and diluted with ten times the volume of ethanol, and the precipitation was started with the slow addition of ether. After further additions of ether, the solution was allowed to stand at 0° for 12 hr. The long yellow needles of the pure $(+)\text{-}[Co(-)\text{-}(stien)_3](ClO_4)_3\cdot 4H_2O$ were collected and washed with ether: 0.46 g, $[\alpha]_D$ +83° (0.1% in methanol). Fractional crystallization of this compound did not change the rotation. *Anal.* Calcd for $C_{36}H_{56}N_6O_{16}Cl_3Co$: C, 47.3, H, 5.2; N, 7.9; Cl, 10.0. Found: C, 47.3; H, 5.3; N, 8.2; Cl, 10.6.

To the combined filtrates from the first filtration was added sodium perchlorate (4 g) in water (300 ml), and the resulting solid was filtered. It was taken up in acetone and filtered, and the solution was evaporated to give a dark brown solid gum from which bright orange crystals were induced to form by the addition of ethanol (5 ml). These were collected and washed quickly with ethanol (5 ml) and then with ether. The crystals (0.4 g) thus obtained were the almost pure $(-)\text{-}[Co(-)\text{-}(stien)_3](ClO_4)_3$ complex. It was recrystallized in an identical manner to that given for the (+) isomer and, unlike the latter, deposited large yellow blocks: 0.24 g, $[\alpha]_D$ −490° (0.1% in methanol). This rotation did not change on fractional crystallization. *Anal.* Calcd for $C_{36}H_{48}N_6O_{12}Cl_3Co$: C, 50.8; H, 4.9; N, 8.5; Cl, 10.7. Found: C, 50.8; H, 5.1; N, 8.4; Cl, 10.6.

We have worked up all the filtrates from this reaction and have obtained a further 0.45 g of the tris compound which consisted of 96% of the (+) isomer. Thus in the preparation, the (+) isomer is formed in higher proportions and corresponds to the isomer first isolated by Lifschitz and Bos[45] using cobalt chloride in ethanol and which Gillard[27] assumed was the more abundant species. Despite the use of activated charcoal, however, these ratios of isomers do not appear to represent the thermodynamic proportions. These seem to be controlled at least in part by virtue of the lower solubility of the chloride salt of the $(+)\text{-}[Co(-)\text{-}(stien)_3]^{3+}$ ion in alcohols, which leads to a displacement of the ratio of isomers in solution. For example, we have repeated the above preparation under similar

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[42] T. G. Appleton and J. R. Hall, *Inorg. Chem.*, **9**, 1800 (1970).

[43] O. F. Williams and J. C. Bailar, *J. Amer. Chem. Soc.*, **81**, 4464 (1959).

[44] I. Lifschitz and J. G. Bos, *Recl. Trav. Chim. Pays Bas*, **59**, 173 (1940).

[45] I. Lifschitz and J. G. Bos, *ibid.*, **59**, 407 (1940).

conditions using cobalt perchlorate instead of cobalt acetate and have obtained exclusively the (−)-[Co(−)-(stien)$_3$](ClO$_4$)$_3$ complex.

Equilibration Studies. We have used three methods of equilibration, all of which gave similar results. The first involved equilibration, under nitrogen, of boiling solutions of the two complexes in the presence of a small amount (1% by weight) of a 3:1 ratio of (−)-stien and cobalt(II) perchlorate. The second involved the use of a 1:1 molar ratio of (−)-stien and the respective complex to catalyze the reaction in boiling methanol. The last involved charcoal, and we describe the method below.

Samples (0.05 g) of the (+)-[Co(−)-(stien)$_3$](ClO$_4$)$_3\cdot$4H$_2$O and (−)-[Co(−)-(stien)$_3$](ClO$_4$)$_3$ complexes were refluxed in methanol (50 ml) in the presence of activated charcoal (0.01 g) for 90 min. The circular dichroism spectra of the filtered solutions showed that both contained predominantly the (−)-[Co(−)-(stien)$_3$]$^{3+}$ ion, but because of the presence of an unidentified decomposition product, with apparently much weaker circular dichroism in the visible region, the exact proportions could not be determined. However, in similar experiments where solutions of (+)-[Co(−)-(stien)$_3$](ClO$_4$)$_3\cdot$4H$_2$O were refluxed for 30, 60 and 240 min, and the corresponding solutions were pumped to dryness, and the solid complexes were isolated by washing the residues with small volumes of ethanol–ether (1:1) to remove the side product, the pure tris complexes thus obtained had circular dichroism spectra which showed the presence of 20, 80 and 100% of (−)-[Co(−)-(stien)$_3$](ClO$_4$)$_3$, respectively. Equilibration of (−)-[Co(−)-(stien)$_3$](ClO$_4$)$_3$ gave no evidence of the presence of the (+) complex. These presumably are not true equilibrium proportions, because the two isomers probably have different rates of decomposition but there is no doubt that, in all the various experiments, the (−)-[Co(−)-(stien)$_3$]$^{3+}$ ion produced no detectable amounts of the (+)-[Co(−)-(stien)$_3$]$^{3+}$ ion, and the (+)-[Co(−)-(stien)$_3$]$^{3+}$ ion isomerized to the almost exclusive production of the (−)-[Co(−)-(stien)$_3$]$^{3+}$ ion.

***trans*-[Co(−)-(stien)$_2$Cl$_2$]ClO$_4\cdot$H$_2$O.** Cobalt chloride hexahydrate (1.2 g) and (−)-stilbenediamine (2.1 g) were dissolved in methanol (100 ml) and air was drawn through the brown solution for 3 hr. Hydrochloric acid (1 ml, 12 *M*) was added and the solution was pumped to dryness to give a green residue. This was extracted with acetone and excess aqueous sodium perchlorate was added to the solution, whereupon green crystals of *trans*-[Co(−)-(stien)$_2$Cl$_2$]ClO$_4$ formed. These were collected and washed with water. Recrystallization was effected by taking up the solid in acetone wherefrom the complex formed as long green needles after the addition of two volumes of water: 1.5 g, [α]D +21° (0.05% in methanol). *Anal.* Calcd for $C_{28}H_{34}N_4O_5Cl_3Co$: C, 50.0; H, 5.1; N, 8.3; Cl, 15.8. Found: C, 50.1; H, 5.1; N, 8.3; Cl, 16.0.

***trans*-[Co*R*,*R*(chxn)$_2$Cl$_2$]ClO$_4$.** The preparation of *trans*-[Co*R*,*R*-(chxn)Cl$_2$)]Cl was the same as that described by Treptow,[46] except that the [Co*R*,*R*(chxn)$_3$]Cl$_3$ salt was removed by eluting the mixture of complexes from a Dowex 50W X8 (H+) resin with 0.4 *M* hydrochloric acid in methanol. The trans compound came off first. The solution was evaporated to dryness and taken up in a small volume of 3 *M* hydrochloric acid; the deep green crystals of the *trans*-[Co-*R*,*R*(chxn)$_2$Cl$_2$]ClO$_4$ were slowly formed after the addition of 1 ml of concentrated perchloric acid. The compound had an identical circular dichroism spectrum in methanol solution as that reported by Treptow. *Anal.* Calcd for $C_{12}H_{28}N_4O_4Cl_3Co$: C, 31.5; H, 6.2; N, 12.2; Cl, 23.3. Found: C, 31.5; H, 6.2; N, 12.1; Cl, 23.5.

***trans*-[Co*R*,*R*(bn)$_2$Cl$_2$]ClO$_4$.** *rac*-2,3-Butanediamine was prepared and resolved by methods described elsewhere.[20] The diastereoisomer of (−)-tartaric acid and (−)-2,3-diaminobutane (1.85 g, αD −0.89°, 5% in water) was dissolved in hot water (5 ml) and potassium chloride (0.4 g) in water (5 ml) was added. After cooling, the potassium hydrogen tartarate was filtered and the solution was neutralized with lithium carbonate (0.4 g). Cobalt chloride hexahydrate (0.63 g) in methanol (50 ml) was added to the neutralized solution, which became a deep brown color after air was passed through it for 3 hr. The solution turned pink when hydrochloric acid (2 ml, 12 *M*) was added after this time. The solution was evaporated down on a steam bath, and when perchloric acid (1 ml, 12 *M*) was added to the small volume, green crystals slowly began to deposit. After a day these were collected and washed with cold perchloric acid (10 ml, 4 *M*). They were recrystallized from methanol by the addition of ether to give fine green needles of the *trans*-[Co*R*,*R*(bn)$_2$Cl$_2$]ClO$_4$ complex: 0.30 g, [α]D −146° (0.05% in methanol). More complex may be obtained by letting the reaction mixture stand for a longer time. In water solution the complex has a marked preference for the cis configuration, though it appears to be conveniently stable in methanol. *Anal.* Calcd for $C_8H_{20}N_4O_4Cl_3Co$: C, 23.7; H, 6.0; N, 13.8; Cl, 26.3. Found: C, 23.4; H, 6.3; N, 13.7; Cl, 26.2.

***trans*-[Co*R*(pn)$_2$Cl$_2$]ClO$_4$.** (−)-Propylenediamine was resolved to the same degree of optical purity as that described elsewhere.[47] *trans*-[Co*R*(pn)$_2$Cl$_2$]Cl$\cdot$H$_5$O$_2$Cl was prepared by the method of Werner and Frohlich[48] The perchlorate salt was obtained by adding concentrated perchloric acid to a concentrated aqueous solution of the chloride salt. It was recrystallized from methanol by the addition of ether: [α]D −190° (0.05% in methanol). *Anal.* Calcd for $C_6H_{20}N_4O_4Cl_3Co$: C, 19.1; H, 5.3; N, 14.8. Found: C, 19.1; H, 5.2; N, 14.8.

***trans*-(Cl$_2$)-[Co*R*pn(NH$_3$)$_2$Cl$_2$]ClO$_4$.** This compound was prepared by essentially the same method as described by Hawkins, Larsen, and Olsen,[49] except that perchloric acid was used instead of sulfuric acid used in the preparation of the bisulfate salt. It was recrystallizated from methanol by the addition of ether: [α]D −100° (0.05% in methanol). *Anal.* Calcd for $C_3H_{16}N_4O_4Cl_3Co$: C, 10.7; H, 4.8; N, 16.6; Cl, 31.5. Found: C, 10.9; H, 5.0; N, 16.5; Cl, 31.5.

***trans*-[Co*R*,*R*(dmtn)$_2$Cl$_2$]ClO$_4$.** (+)-2,4-Diaminopentane dihydrochloride (1.0 g, [α]D +17°) in water (5 ml) was neutralized with sodium carbonate (0.61 g) and then added to cobalt chloride hexahydrate (0.68 g) in methanol (50 ml). Air was passed through the solution for 1 hr. The brown methanol solution was then evaporated under reduced pressure, and the residue taken up in water (10 ml). After the addition of hydrochloric acid (5 ml, 12 *M*) and perchloric acid (5 ml, 12 *M*), the solution was heated on a steam bath for 10 min and then allowed to cool to room temperature. The fine green needles of *trans*-[Co*R*,*R*(dmtn)$_2$Cl$_2$]ClO$_4$ were collected and washed with water, ethanol, and finally with ether. They were recrystallized from hot water (25 ml) by the addition of hydrochloric acid (2 ml, 12 *M*) and perchloric acid (2 ml, 12 *M*): 0.7 g, [α]D −280° (0.2% in methanol). *Anal.* Calcd for $C_{10}H_{28}N_4O_4Cl_3Co$: C, 27.7; H, 6.5; N, 12.9; Cl, 24.5. Found: C, 27.7; H, 6.3; N, 12.9; Cl, 24.7.

***cis*-β-*R*,*R*;*S*,*S*-[Co-2,3,2-tet(ox)]Cl.** *trans*-*R*,*S*-[Co-2,3,2-tetCl$_2$]Cl (11 g), prepared by methods given elsewhere,[50] was added to a solution of oxalic acid (4.5 g) and lithium carbonate (3.0 g) and the solution was boiled for 10 min. The red crystals were precipitated by the addition of ethanol followed by acetone, collected, and washed with acetone (11 g). We have established its unsymmetrical cis-β configuration from the pmr spectrum in D$_2$O–1% DCl, which shows a clear, well separated amino proton signal (checked by deuteration) of area representing one proton. This establishes the cis-β geometry, since for the symmetrical cis-α geometry the amino protons would occur in areas representing two protons. *Anal.* Calcd for $C_9H_{20}N_4O_4ClCo$: C, 31.5; H, 5.9; N, 16.3. Found: C, 31.0; H, 6.0; N, 16.1.

(−)-*cis*-β-*S*,*S*-[Co-2,3,2-tet(ox)]ClO$_4$. We have resolved the *cis*-β-*R*,*R*;*S*,*S*-[Co-2,3,2-tet(ox)]Cl complex by means of the (+)-α-bromocamphor-π-sulfonate diastereoisomer. Although the material we have obtained is probably optically pure, the method is not very efficient and we refer to a better method given in the literature:[28] [α]D −495° in water. *Anal.* Calcd for $C_9H_{20}N_4O_8ClCo$: C, 26.5; H, 5.0; N, 13.8. Found: C, 26.7; H, 4.9; N, 13.9.

***trans*-*S*,*S*-[Co-2,3,2-tetCl$_2$]ClO$_4$.** *cis*-β-*S*,*S*-[Co-2,3,2-tet(ox)]ClO$_4$ (0.16 g, [α]D −495°) was dissolved in hydrochloric acid (10 ml, 12 *M*) and the solution was heated on a steam bath for 3 hr. To this resulting violet solution was added perchloric acid (1 ml, 12 *M*) and the solution was allowed to stand overnight. The green crystals of *trans*-*S*,*S*-[Co-2,3,2-tetCl$_2$]ClO$_4$ were collected and washed with acetone: 0.1 g, [α]D −120° (0.05% in methanol). *Anal.* Calcd for $C_7H_{20}N_4O_4Cl_3Co$: C, 21.5; H, 5.2; N, 14.4; Cl, 27.3. Found: C, 22.0; H, 5.2; N, 14.6; Cl, 27.3.

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(46) R. S. Treptow, *Inorg. Chem.*, **5**, 1593 (1966).

(47) F. P. Dwyer, F. L. Garvan, and A. Schulman, *J. Amer. Chem. Soc.*, **81**, 290 (1959).

(48) A. Werner and A. Frohlich, *Ber.*, **40**, 2225 (1907).

(49) C. J. Hawkins, E. Larsen, and I. I. Olsen, *Acta Chem. Scand.*, **19**, 1915 (1965).

(50) B. Bosnich, R. D. Gillard, E. D. McKenzie, and G. A. Webb, *J. Chem. Soc. A*, 1331 (1966).