

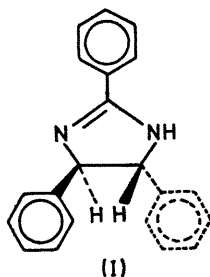
## The Dynamic-coupling Basis of the Conformational Optical Activity of Chelated Metal Complexes

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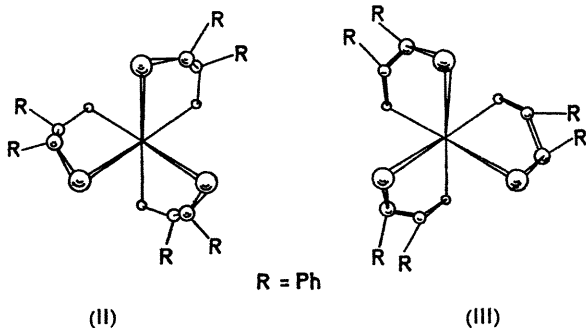
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**Summary** The absolute configuration of (–)-stilbene diamine is shown to be (*R,R*), and the c.d. spectra of the cobalt(III) complexes with this ligand are found to support the dynamic-coupling or polarisability mechanism for the conformational optical activity due to chirally-puckered chelate rings in metal complexes, but not the static field mechanism in which that optical activity arises from the charges of the ligand atoms.

RECENTLY it has been suggested that the optical activity of chiral metal complexes with an octahedral parentage is due to a series of superposed perturbations arising from the dissymmetric substitution pattern, and sector rules were proposed for complexes with an effective octahedral,



tetragonal, or trigonal chromophoric symmetry.<sup>1</sup> A chirally-puckered diamine chelate ring in the  $\text{CoN}_6$  chromophore gives a conformational optical activity<sup>2-4</sup> following the octahedral sector rule, and this effect is superposed, in the corresponding  $[\text{Co}(\text{diamine})_3]^{3+}$  complex, upon the configurational optical activity which follows the trigonal sector rule or, in the analogous *trans*- $[\text{Co}(\text{diamine})_2\text{X}_2]^{3+}$  complex, upon the specifically-tetragonal optical activity.<sup>1</sup>



As a basis for the sector rules two mechanisms generating optical-activity were considered,<sup>1</sup> the static-field<sup>5</sup> and the dynamic coupling<sup>6</sup> treatment. According to the first mechanism the static charges of the substituents mix the electric-dipole with the magnetic-dipole transitions of the symmetric metal-ion chromophore,<sup>7</sup> whereas in the second mechanism the moment of a metal-ion transition couples

with a moment induced by the radiation field in the substituent, depending upon the polarisability of the latter.

In order to distinguish between the two mechanisms we have obtained the c.d. spectra of cobalt(III) complexes with (–)-stilbenediamine (*l*-stein)<sup>8</sup> which contains groups, the benzene rings, with a large polarisability<sup>9</sup> (Figures 1 and 2).

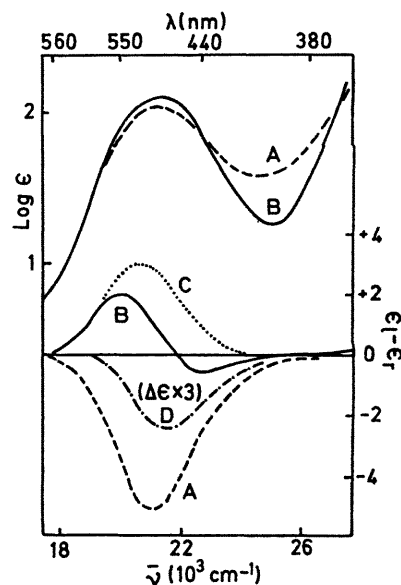


FIGURE 1. The absorption spectra (upper curves) and c.d. spectra (lower curves) of (A)  $\Delta(\lambda\lambda\lambda)$ -(-)- $[\text{Co}(l\text{-stien})_3]^{3+}$  (II) and (B)  $\Lambda(\lambda\lambda\lambda)$ -(+)- $[\text{Co}(l\text{-stien})_3]^{3+}$  (III). Curve (C) represents the configurational optical activity of three hypothetically-planar *l*-stien chelate rings in a cobalt (III) complex with the  $\Delta$ -configuration, and is given by the mean of the difference between the c.d. curves (A) and (B). Curve (D) represents the conformational optical activity of a single *l*-stien chelate ring in a  $\text{CoN}_6$  complex, obtained as one-sixth of the sum of the c.d. curves (A) and (B).

The absolute configuration of (–)-stilbenediamine was determined as (*R,R*) by chemical correlation with (–)-*iso*-amarine (I) which gives a c.d. spectrum closely resembling that of (*R,R*)-(+)-*trans*-stilbene oxide.<sup>10</sup> The exciton analysis of the c.d. spectrum of (–)-*iso*-amarine by the method previously described<sup>10</sup> confirms the (*R,R*) configuration (I).

The conformational analysis of chelate rings indicates<sup>11</sup> that a 1,2-diamine with the *R*-configuration gives a  $\lambda$ -skew ring<sup>12</sup> (Figure 3) and forms two tris-complexes, the thermodynamically more stable *lel*-isomer,  $\Delta(\lambda\lambda\lambda)$  and the less stable *ob*-isomer,  $\Lambda(\lambda\lambda\lambda)$ . Of the two  $[\text{Co}(l\text{-stien})_3]^{3+}$  complexes the (–)-isomer is the more stable thermodynamically, representing the *lel*-form,  $\Delta(\lambda\lambda\lambda)$  (II), and the (+)-isomer has the *ob*-form,  $\Lambda(\lambda\lambda\lambda)$  (III). The c.d. curves of the two  $[\text{Co}(l\text{-stien})_3]^{3+}$  isomers give a normal configurational

optical activity for five-membered chelate rings,<sup>1-4</sup> *i.e.* positive for the  $\Lambda$ -configuration, but the conformational optical activity is negative, whereas alkyl-substituted (*R*)-1,2(*R*)-1,2-diamines give a positive conformational effect<sup>2-4</sup>

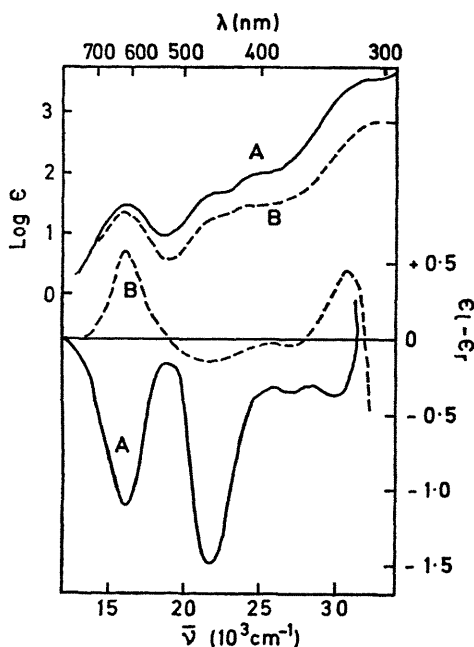


FIGURE 2. The absorption spectra (upper curves) and c.d. spectra (lower curves) of (A)  $\text{trans}[\text{Co}(\text{l-stien})_2\text{Cl}_2]^+$  and (B)  $\text{trans}[\text{Co}(\text{l-pn})_2\text{Cl}_2]^+$ .

(Figure 1). The c.d. of  $\text{trans}[\text{Co}(\text{l-stien})_2\text{Cl}_2]^+$  is negative for all of the accessible  $d \rightarrow d$  transitions (Figure 2), indicating that the conformational optical activity is negative and relatively large, entirely overlying the tetragonal optical-activity which, for a (*R*)-1,2-diamine, is expected<sup>1</sup> to be positive and negative respectively for the  $A_{1g} \rightarrow E_g$  and  $A_{1g} \rightarrow A_{2g}$  tetragonal components of the octahedral  $A_{1g} \rightarrow T_{1g}$  transition.

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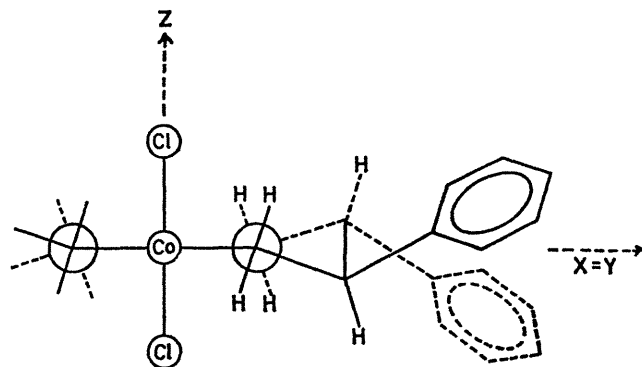


FIGURE 3. The preferred  $\lambda$ -conformation of a (*R,R*)-(-)-stilbene-diamine chelate ring and the co-ordinate frame of the octahedral sector rule (eq. 1). The X-axis is directed along the upper, and the Y-axis along the lower Co-N bond of the *l*-stien chelate ring.

These observations indicate that the conformational optical-activity following the octahedral sector rule is dominated by the phenyl groups in stilbene diamine complexes of cobalt(III). The C-N, C-C, and C-H bonds of a (*R,R*)-(-)-stilbene diamine chelate ring, like the corresponding bonds of a (*R*)-(-)-propylene diamine (pn) ring,<sup>2-4</sup> lie in regions where the substituent co-ordinate function,<sup>1</sup> of the octahedral sector rule is positive, giving

$$F(\text{Oh}) = [\text{XYZ}(\text{X}^2 - \text{Y}^2)(\text{Y}^2 - \text{Z}^2)(\text{Z}^2 - \text{X}^2)] \quad (1)$$

a positive induced optical activity, whereas the phenyl groups are disposed in regions where that function is negative and give a negative induced rotational strength (Figure 3.)

The phenyl group has a substantially larger polarisability<sup>9</sup> ( $\bar{\alpha} = 10.32 \text{ \AA}^3$ ) than a C-C ( $\bar{\alpha} = 0.64 \text{ \AA}^3$ ) or a C-H group ( $\bar{\alpha} = 0.65 \text{ \AA}^3$ ), but it is unlikely that the benzene nuclei of a stilbenediamine chelate ring carry a charge significantly larger than that of the carbon and hydrogen atoms of the chelate ring. Accordingly the present results support the dynamic-coupling or polarisability mechanism<sup>6</sup> for the conformational optical activity of chiral metal complexes following the octahedral sector rule shown by equation (1).

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