deuterium isotope effect for the Ru(II)–Ru(III) self-exchange reactions is not known.

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The Exciton Circular Dichroism and the Absolute Configurations of Molecules Containing Nonidentical Chromophores. The Cases of the Bis(*o*-phenanthroline)-2,2′-bipyridylruthenium(II) and Bis(2,2′-bipyridyl)-*o*-phenanthrolineruthenium(II) Ions

BY B. BOSNICH

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The exciton theory of optical activity has been applied to dissymmetric systems containing coupled nonidentical chromophores. Calculations have been carried out in order to determine the expected absorption and circular dichroism spectra resulting from the coupling of the long-axis-polarized transitions of the *o*-phenanthroline (phen) and the 2,2′-bipyridyl (bipy) ligands in the two systems $\mathrm{Ru(phen)_2bipy^{2+}}$ and $\mathrm{Ru(bipy)_2phen^{2+}}$. For the purpose of testing the theory and its assumptions, the two ions $\mathrm{Ru(phen)_2bipy^{2+}}$ and $\mathrm{Ru(bipy)_2phen^{2+}}$ have been prepared and resolved, and their absorption and circular dichroism spectra have been recorded. It has been found that the correlation between theory and experiment is satisfactory and allows for the determination of the absolute configurations of these molecules.

The purely spectroscopic methods of determining the absolute configurations of dissymmetric molecules rely only on a knowledge of the polarization directions of particular electronic transitions of the molecule. This so-called coupled-oscillator method has been developed for and applied to a variety of systems since it was first set out classically by Kuhn[1] and modified within the formalism of the exciton theory by Moffitt.[2] That the method offers reliable means of arriving at the absolute configurations of inorganic complexes[3–6] of simple organic molecules[7,8] and of regular oligomers and polymers[9,10] has been amply verified by experiment. In all of these systems, however, the exciton exchange is assumed to occur between a set of essentially identical chromophores and formally no account has been taken of the possibility of mixing between nondegenerate transitions, although it has been generally recognized as a possible complication if the system is not judiciously chosen.[11]

It is the purpose of this article to outline briefly the methods for dealing with the nondegenerate problem, to apply it in detail to a number of representative examples, and to show that the treatment is necessary for the determination of the absolute configurations of the ions $\mathrm{Ru(phen)_2bipy^{2+}}$ and $\mathrm{Ru(bipy)_2phen^{2+}}$.

I. The General Formulation

The formalism of the nondegenerate problem follows closely that used for degenerate systems. Let the system contain n residues, whose ground-state wave functions are represented by χ_i; then the ground-state wave function, Ψ_0, for the total system is given by the product

$$\Psi_0 = \chi_1\chi_2\chi_3\ldots\chi_i\ldots\chi_n \tag{1}$$

in which any number of the functions, χ, may or may not be the same. We shall suppose for the present purposes that we need consider only one excited state of the individual chromophores of the assembly. This allows us to write the (singly) excited state wave functions, Φ_i, of the system in the following way

$$\Phi_1 = \chi_1'\chi_2\chi_3\ldots\chi_n,\ \Phi_2 = \chi_1\chi_2'\chi_3\ldots\chi_n,\ \text{etc.}$$

or more generally

$$\Phi_i = \chi_1\chi_2\chi_3\ldots\chi_i'\ldots\chi_n \tag{2}$$

where the primes represent excited-state functions. The total wave function, Ψ_j, corresponding to the jth excited state of the assembly, may therefore be expressed as a linear combination of the unperturbed singly excited-state wave functions, Φ_i, with apposite

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mixing coefficients, C_{ij}, referring to the ith function of the jth level

$$\Psi_j = C_{1j}\Phi_1 + C_{2j}\Phi_2 + \ldots + C_{ij}\Phi_i + \ldots + C_{nj}\Phi_j \quad (3)$$

where $j = 1, 2, 3, \ldots n$. By applying the variation treatment one obtains a set of n simultaneous equations which may be represented by

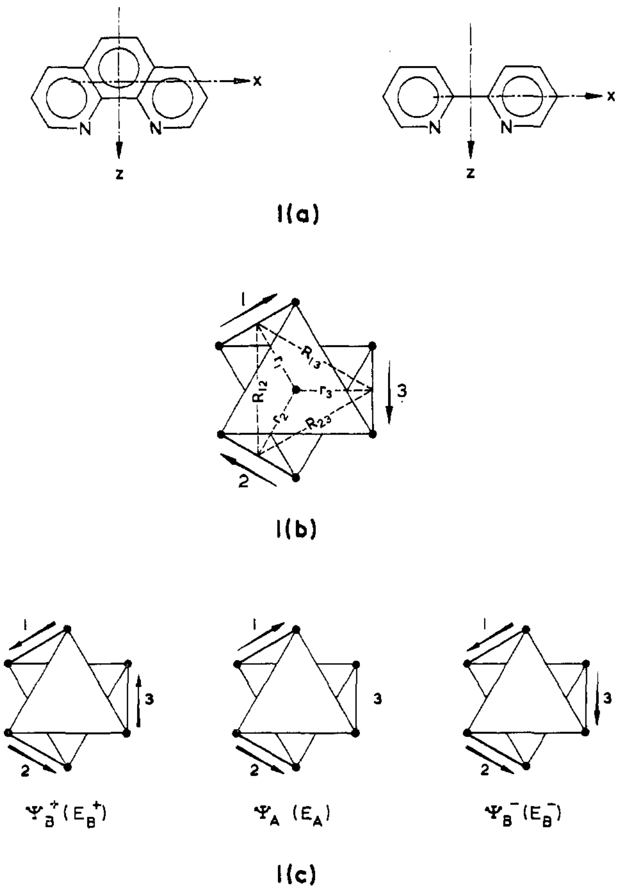
$$\sum_{=1}^{n} [H_{ij} - S_{ij}(H_{00} + E)]C_j = 0; \qquad i = 1, 2, 3, \ldots, n \quad (4)$$

where $H_{ij} = \langle\Phi_i|H|\Phi_j\rangle$, H being the Hamiltonian of the system, $S_{ij} = \langle\Phi_i|\Phi_j\rangle$, and E is the appropriate energy. In order that the ground-state interactions may be considered and so that the energies may be expressed as transition energies, the term $H_{00} = \langle\Psi_0|H|\Psi_0\rangle$ has been included. For nontrivial solutions to the simultaneous equations the secular determinant is set to zero

$$|H_{ij} - S_{ij}(H_{00} + E)| = 0 \quad (5)$$

where provided normalized basis functions are used, $S_{ij} = 1$ when $i = j$, and where it is generally assumed that $S_{ij} = 0$ when $i \neq j$. The solution to this problem gives n eigenfunctions and, correspondingly, n eigenvalues and allows for the calculation of the dipole and rotational strengths of the system in terms of the empirically known spectroscopic properties of the individual constituent chromophores.

This specifies the formalism of the problem and we now turn to the calculation of the spectroscopic properties of the $Ru(phen)_2bipy^{2+}$ ion.



I(a) I(b) I(c)

Figure 1.—In (a) the *o*-phenanthroline and 2,2′-bipyridyl molecules are shown together with the definition of their short (z) and long (x) axes. The central figure (b) shows the geometry of the $Ru(phen)_2bipy^{2+}$ and $Ru(bipy)_2phen^{2-}$ ions and the definitions of the various geometric parameters used in the calculations. The arrows represent the directions of the three long-axis polarized $\pi \rightarrow \pi^*$ transitions in their initial choice of phases. The bottom three figures (c) are pictorial representations of the three exciton coupling modes where the relative lengths of the arrows have, for convenience, been made equal. It will be seen that the combination on the left involves a left-handed helical displacement of charge along and about the axes perpendicular to the twofold axis and that the combination shown in the middle figure involves a right-handed helical displacement of charge along and about the twofold axis. These two modes should, as has been calculated, give rise to negative and positive circular dichroism, respectively. The combination on the right is of mixed chirality which may be seen by taking the arrows in pairs. The pairs 1, 3 and 2, 3 involve right-handed helical displacements of charge while the pair 1, 2 involves a left-handed helical displacement of charge. To a certain degree of simplification, it therefore can be seen why the expression for R_B^- contains two positive terms and a negative term.

II. The Absorption and Circular Dichroism Spectra of the $Ru(phen)_2bipy^{2+}$ Ion

The $\pi \rightarrow \pi^*$ transitions of the *o*-phenanthroline molecule and the planar 2,2′-bipyridyl molecule are either short-axis (z) or long-axis (x) polarized (Figure 1). Polarized crystal spectra of phenanthrene[12-14] and biphenyl,[15,16] together with molecular orbital calculations and circular dichroism data,[4,5,17] strongly suggest that the long-axis polarized transition of *o*-phenanthroline occurs at around 38,000 cm^{-1} and that the long-axis polarized transition of 2,2′-bipyridyl occurs at around 34,000 cm^{-1}. In both systems the short-axis polarized transitions occur at somewhat lower energies, although they extend to higher energies and lie underneath the generally more intense long-axis polarized transitions. Upon complex formation, the $\pi \rightarrow \pi^*$ transitions of the free ligands remain largely unmodified[17] except that they couple by exciton exchange interactions.[4,5] Because of the particular geometry of the octahedron, the short-axis polarized transitions of the complexed bidentate ligands can couple to produce only transition dipole moments in the zero order and therefore cannot give rise to exciton circular dichroism; but the long-axis polarized transitions of the chromophores are so disposed as to create parallel electric and magnetic transition dipole moments during the absorption of light and hence give rise to zero-order rotational strengths. Depending on the magnitude of the transition dipole moments of the individual chromophores and their particular geometric relationship with each other, the zero-order rotational strength produced by the exciton interaction can be extremely large compared

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with the other sources of optical activity. It is because of this fact that we shall concern ourselves with only the long-axis polarized transitions.

The ground-state wave function, Ψ_0, for the system Ru(phen)$_2$bipy^{2+} is written

$$\Psi_0 = \chi_1\chi_2\varphi_3 \tag{6}$$

where χ_1 and χ_2 refer to the ground-state wave functions of complexed *o*-phenanthroline molecules 1 and 2, respectively, and where φ_3 refers to the ground-state wave function of the complexed 2,2′-bipyridyl molecule (Figure 1). Similarly the (singly) excited-state wave functions for the system are written as

$$\begin{aligned}\Phi_1 &= \chi_1'\chi_2\varphi_3\\ \Phi_2 &= \chi_1\chi_2'\varphi_3\\ \Phi_3 &= \chi_1\chi_2\varphi_3'\end{aligned} \tag{7}$$

where the primes represent the excited-state wave functions of the long-axis polarized $\pi \rightarrow \pi^*$ transitions. By recognizing the symmetry (C$_2$) of the problem and substituting in eq 5, the secular determinant for the system becomes

$$\begin{vmatrix} H_{11} + H_{12} - H_{00} - E & 0 & \sqrt{2}H_{13} \\ 0 & H_{11} - H_{12} - H_{00} - E & 0 \\ \sqrt{2}H_{13} & 0 & H_{33} - H_{00} - E \end{vmatrix} = 0 \tag{8}$$

We shall assume that, to a first approximation, the Ru(phen)$_2$bipy^{2+} ion can be described as a weakly coupled system where only electrostatic coupling of the chromophores need be considered. This allows us to split the total Hamiltonian, H, of the system in the following way

$$H = H_1 + H_2 + H_3 + \sum_{i<j}^{3} \vartheta_{ij}$$

where H_1 and H_2 are the appropriate Hamiltonians for *o*-phenanthroline molecules 1 and 2, respectively, and where, similarly, H_3 refers to the 2,2′-bipyridyl molecule. The operator ϑ_{ij} refers to the interaction between the ith and jth molecules of the system. By making this assumption we may simplify the determinant in eq 8, and as an example we consider the terms in the first row and first column, for which we find

$$\begin{aligned} H_{11} &= \langle \chi_1'\chi_2\varphi_3 | H_1 + H_2 + H_3 + \sum_{i<j}^{3} \vartheta_{ij} | \chi_1'\chi_2\varphi_3 \rangle \\ &= \langle \chi_1' | H_1 | \chi_1' \rangle + \langle \chi_2 | H_2 | \chi_2 \rangle + \langle \varphi_3 | H_3 | \varphi_3 \rangle + \\ &\quad \langle \chi_1'\chi_2 | \vartheta_{12} | \chi_1'\chi_2 \rangle + \langle \chi_1'\varphi_3 | \vartheta_{13} | \chi_1'\varphi_3 \rangle + \\ &\quad \langle \chi_2\varphi_3 | \vartheta_{23} | \chi_2\varphi_3 \rangle \end{aligned} \tag{9}$$

provided orthonormal functions are used. In eq 9, the first term, $\langle \chi_1' | H_1 | \chi_1' \rangle = E'$, represents the excited-state energy of the long-axis polarized $\pi \rightarrow \pi^*$ transition of *o*-phenanthroline molecule 1, the terms $\langle \chi_2 | H_2 | \chi_2 \rangle = E_2$ and $\langle \varphi_3 | H_3 | \varphi_3 \rangle = E_3$ refer to the ground-state energies of *o*-phenanthroline molecule 2 and the 2,2′-bipyridyl molecule, respectively, the terms $\langle \chi_1'\chi_2 | \vartheta_{12} | \chi_1'\chi_2 \rangle$ and $\langle \chi_1'\varphi_3 | \vartheta_{13} | \chi_1'\varphi_3 \rangle$ refer to the interactions of the static excited-state multipole moment of molecule 1 with the static ground-state multipole moments of molecules 2 and 3, respectively, and, finally, the last term, $\langle \chi_2\varphi_3 | \vartheta_{23} | \chi_2\varphi_3 \rangle$, represents the interaction of the static ground-state multipole moments of molecules 2 and 3. By similar methods

$$H_{12} = \langle \chi_1'\chi_2\varphi_3 | H_1 + H_2 + H_3 + \sum_{i<j}^{3} \vartheta_{ij} | \chi_1\chi_2'\varphi_3 \rangle = \langle \chi_1'\chi_2 | \vartheta_{12} | \chi_1\chi_2' \rangle = V_{12}$$

and

$$\begin{aligned} H_{00} = {} & \langle \chi_1 | H_1 | \chi_1 \rangle + \langle \chi_2 | H_2 | \chi_2 \rangle + \langle \varphi_3 | H_3 | \varphi_3 \rangle + \\ & \langle \chi_1\chi_2 | \vartheta_{12} | \chi_1\chi_2 \rangle + \langle \chi_1\varphi_3 | \vartheta_{13} | \chi_1\varphi_3 \rangle + \langle \chi_2\varphi_3 | \vartheta_{23} | \chi_2\varphi_3 \rangle \end{aligned}$$

where V_{12} represents the interaction between the transition dipole moments of *o*-phenanthroline molecules 1 and 2, where $\langle \chi_1 | H_1 | \chi_1 \rangle = E_1$ is the ground-state energy of *o*-phenanthroline molecule 1, and where the last three terms refer to the ground-state multipole interactions. The first term of (8) thus reduces to

$$H_{11} + H_{12} - H_{00} - E = \Delta E_1 + V_{12} - E$$

where $\Delta E_1 = E_1' - E_1$ is the transition energy of the long-axis polarized $\pi \rightarrow \pi^*$ transition of *o*-phenanthroline molecule 1. It has been assumed that the difference between the static multipole moments of the excited states of the molecules and the static multipole moments of the ground states of the molecules is small and can be neglected. This is a usual assumption although the justification for it is not always strong. However, it will not affect the outcome of the semiquantitative arguments we wish to pursue here.

With these assumptions and carrying out the calculations for the other terms, the determinant in eq 8 reduces to

$$\begin{vmatrix} \Delta E_1 + V_{12} - E & 0 & \sqrt{2}V_{13} \\ 0 & \Delta E_1 - V_{12} - E & 0 \\ \sqrt{2}V_{13} & 0 & \Delta E_3 - E \end{vmatrix} = 0 \tag{10}$$

where an obvious extension of the symbolism has been employed. The only unknown quantities in the determinant of eq 10 are V_{13} and V_{12} which are readily calculated; the transition energies ΔE_1 and ΔE_3 are known from experiment. We thus arrive at the eigenvalues E_A, $E_B{}^+$, and $E_B{}^-$, referring to the first three long-axis polarized transitions of the ion Ru(phen)$_2$bipy^{2+}

$$E_A = \Delta E_1 - V_{12}$$

$$E_B{}^+ = \frac{\Delta E_1 + \Delta E_3 + V_{12} + \{(-\Delta E_1 - \Delta E_3 - V_{12})^2 - 4(\Delta E_1\Delta E_3 + \Delta E_3 V_{12} - 2V_{13}{}^2)\}^{1/2}}{2}$$

$$E_B{}^- = \frac{\Delta E_1 + \Delta E_3 + V_{12} - \{(-\Delta E_1 - \Delta E_3 - V_{12})^2 - 4(\Delta E_1\Delta E_3 + \Delta E_3 V_{12} - 2V_{13}{}^2)\}^{1/2}}{2}$$

The corresponding eigenfunctions for E_A, E_B^+, and E_B^-, respectively, are

$$\Psi_A = \frac{1}{\sqrt{2}}(\Phi_1 - \Phi_2)$$

$$\Psi_B^+ = C_1^+\left\{\frac{1}{\sqrt{2}}(\Phi_1 + \Phi_2)\right\} + C_2^+\Phi_3$$

$$\Psi_B^- = C_1^-\left\{\frac{1}{\sqrt{2}}(\Phi_1 + \Phi_2)\right\} + C_2^-\Phi_3$$

where the subscripts A and B refer to the irreducible representations of C_2 under which the functions transform. The constants C_1^+, C_2^+, C_1^-, and C_2^- are the mixing coefficients which, when the functions are orthonormal, have the values

$$C_1^+ = -C_2^- = \frac{-\sqrt{2}V_{13}}{(2V_{13}^2 + L^2)^{1/2}}$$

and

$$C_2^+ = C_1^- = \frac{L}{(2V_{13}^2 + L^2)^{1/2}}$$

where

$$L = \frac{\Delta E_1 + V_{12} - \Delta E_3 - \{(-\Delta E_1 - \Delta E_3 - V_{12})^2 - 4(\Delta E_1\Delta E_3 + \Delta E_3 V_{12} - 2V_{13}^2)\}^{1/2}}{2}$$

It is readily shown that $|C_1^+| = |C_2^-| > |C_2^+| = |C_1^-|$ and that C_2^+ and C_1^- are always negative. Since C_1^+ is greater than C_2^+, the wave function Ψ_B^+, corresponding to the energy E_B^+, is associated with the $\pi \rightarrow \pi^*$ *o*-phenanthroline transition which is mixed with the $\pi \rightarrow \pi^*$ transition of 2,2′-bipyridyl and, similarly, since C_1^- is less than C_2^-, the wave function Ψ_B^-, corresponding to the eigenvalue E_B^-, is associated with the 2,2′-bipyridyl $\pi \rightarrow \pi^*$ transition which is mixed with the $\pi \rightarrow \pi^*$ transition of *o*-phenanthroline. The function Ψ_A, associated with the energy E_A, refers only to the $\pi \rightarrow \pi^*$ transition of *o*-phenanthroline. The values of the coefficients and the three eigenvalues can now be found, provided we can calculate V_{13} and V_{12}.

For this purpose we shall use the point-dipole–point-dipole approximation. This particular approximation is unlikely to be quantitatively sufficient in the present system, since the transition dipole length and the distance between the chromophores are the same order of magnitude; it probably leads to errors of up to 50% in absolute magnitude of the splitting. However, it will give the correct sense of the splittings which is sufficient for our present purposes. We find using this approximation and using the choice of phases shown in Figure 1(b) that

$$V_{12} = V_{21} = \frac{1p_1p_2}{4R_{12}^3}$$

and

$$V_{13} = V_{31} = \frac{1}{R_{13}^3}\left\{\frac{p_1p_3}{2} - \frac{3p_1p_3r_1}{4(r_1 + r_3)^2}\right\}$$

where R_{12} is the distance between the "centers" of the excitation moments of the two *o*-phenanthroline molecules, R_{13} is the distance between the "centers" of the excitation moments of an *o*-phenanthroline molecule and a 2,2′-bipyridyl molecule, r_1 and r_3 are the distances between the center of the ruthenium atom and the "centers" of the transition dipole moments of the *o*-phenanthroline and the 2,2′-bipyridyl molecules, respectively, and p_1 and p_3 refer to the values of the transition dipole moments of the long-axis polarized $\pi \rightarrow \pi^*$ transitions of the *o*-phenanthroline and 2,2′-bipyridyl molecules, respectively. [We note that $p_1 = p_2$, $r_1 = r_2$, $R_{12} = \sqrt{3}r_1$, $R_{13} = \sqrt{r_1^2 + r_3^2 + r_1r_3}$, and $R_{13} = R_{31}$; see Figure 1(b).] Thus the two originally degenerate *o*-phenanthroline transitions are split by exciton interaction and the energies of the final upper states lie in the following decreasing order $E_B^+ > E_A > E_B^-$. This result is shown in Figure 2. We are now left with calculating the dipole and rotational strength associated with each transition.

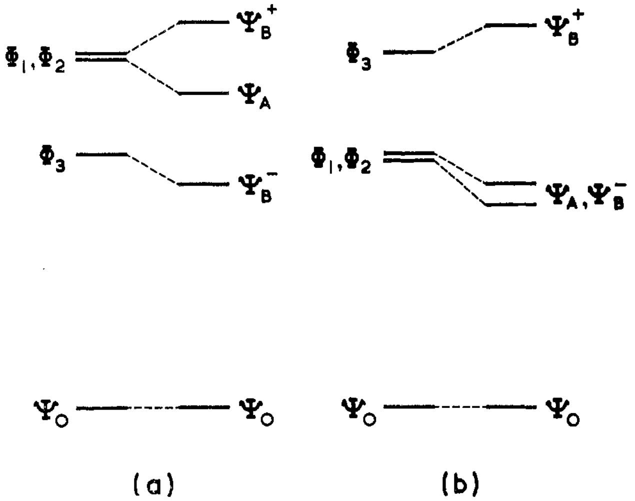

Figure 2.—Schematic energy level diagrams showing the relative energy positions of the four wave functions Ψ_0, Φ_1, Φ_2, and Φ_3 before exciton interaction and the energy positions of the final wave functions Ψ_0, Ψ_B^-, Ψ_A, and Ψ_B^+ after exciton exchange. Scheme (a) refers to the $Ru(phen)_2bipy^{2+}$ ion and scheme (b) refers to the $Ru(bipy)_2phen^{2+}$ ion.

For the transition from the totally symmetric ground-state function, Ψ_0, to the excited-state wave function, Ψ_A, which is polarized along the twofold axis of $Ru(phen)_2bipy^{2+}$, we find the zero-order dipole strength, D_A, and the zero-order rotational strength, R_A, for the particular absolute configuration shown in Figure 1, to be given by

$$D_A = \frac{1}{2}p_1^2$$

and

$$R_A = +\frac{1}{\sqrt{2}}\pi\bar{\nu}_1 r_1 p_1^2$$

where $\bar{\nu}_1$ is the frequency in wave numbers of the long-axis polarized $\pi \rightarrow \pi^*$ transition of the unperturbed (complexed) *o*-phenanthroline molecule and where we note that $r_1 = r_2$, $\bar{\nu}_1 = \bar{\nu}_2$, and $p_1 = p_2$. The transition $\Psi_0 \rightarrow \Psi_B{}^+$, which is polarized in the directions normal to the twofold axis, has, for the particular absolute configuration shown in Figure 1, a zero-order dipole strength, $D_B{}^+$, and a zero-order rotational strength, $R_B{}^+$, given by

$$D_B{}^+ = (C_1{}^+)^2\frac{3}{2}p_1{}^2 + (C_2{}^+)^2p_3{}^2 + C_1{}^+C_2{}^+\sqrt{2}p_1p_3$$

and

$$R_B{}^+ = -(C_1{}^+)^2\frac{1}{\sqrt{2}}\pi\bar{\nu}_1r_1p_1{}^2 - C_1{}^+C_2{}^+\pi\bar{\nu}_1r_1p_1p_3 - C_1{}^+C_2{}^+\pi\bar{\nu}_3r_3p_1p_3$$

where $\bar{\nu}_3$ is the frequency in wave numbers at which the isolated (complexed) 2,2′-bipyridyl $\pi \rightarrow \pi^*$ transition occurs. For the $\Psi_0 \rightarrow \Psi_B{}^-$ transition, which is also polarized in the directions normal to the twofold axis, a similar expression obtains for the dipole strength, $D_B{}^-$, and the rotational strength, $R_B{}^-$, for the absolute configuration in Figure 1, namely

$$D_B{}^- = (C_1{}^-)^2\frac{3}{2}p_1{}^2 + (C_2{}^-)^2p_3{}^2 + C_1{}^-C_2{}^-\sqrt{2}p_1p_3$$

and

$$R_B{}^- = -(C_1{}^-)^2\frac{1}{\sqrt{2}}\pi\bar{\nu}_1r_1p_1{}^2 - C_1{}^-C_2{}^-\pi\bar{\nu}_1r_1p_1p_3 - C_1{}^-C_2{}^-\pi\bar{\nu}_3r_3p_1p_3$$

These three coupling modes are shown pictorially in Figure 1(c).

It will be noted that the conservation laws for both dipole strength and rotational strength hold, as shown by

$$D_A + D_B{}^+ + D_B{}^- = 2p_1{}^2 + p_1{}^2 = p_1{}^2 + p_2{}^2 + p_3{}^2$$

and

$$R_A + R_B{}^+ + R_B{}^- = 0$$

Thus the exciton theory of optical activity predicts that, for the Ru(phen)$_2$bipy^{2+} ion in the absolute configuration shown in Figure 1, the transition $\Psi_0 \rightarrow \Psi_A$ should carry positive circular dichroism and, since $C_1{}^+$ and $C_2{}^+$ are both negative quantities, the $\Psi_0 \rightarrow \Psi_B{}^+$ transition should carry negative circular dichroism. Despite the fact that $C_1{}^-$ and $C_2{}^-$ are of opposite sign, the $\Psi_0 \rightarrow \Psi_B{}^-$ transition will also carry positive circular dichroism, although it will be smaller than that shown by the $\Psi_0 \rightarrow \Psi_B{}^+$ transition.

In Figure 3 we show the absorption and circular dichroism spectra of the (+)-Ru(phen)$_2$bipy^{2+} ion in water solution. The absorption and circular dichroism in the region between 18,000 and 32,000 cm^{-1} most probably is due to three main overlapping sources, the d–d transitions of the ruthenium ion, charge-transfer transitions involving the promotion of electrons from the filled d_ϵ orbitals of the ruthenium to the vacant π^* orbitals of the ligands, and, toward the higher energy end, short-axis polarized $\pi \rightarrow \pi^*$ transitions of the ligands. Except for the fact that the small, positive circular dichroism shoulder around 20,000 cm^{-1} possibly represents components of the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition of the ruthenium ion, these transitions are not strictly relevant to the present discussion and we shall not pursue a discussion of them here. It is in the region between about 32,000 and 43,000 cm^{-1}, where the long-axis polarized transitions occur, that the absorption spectrum and circular dichroism spectrum should show the characteristics predicted by the exciton theory.

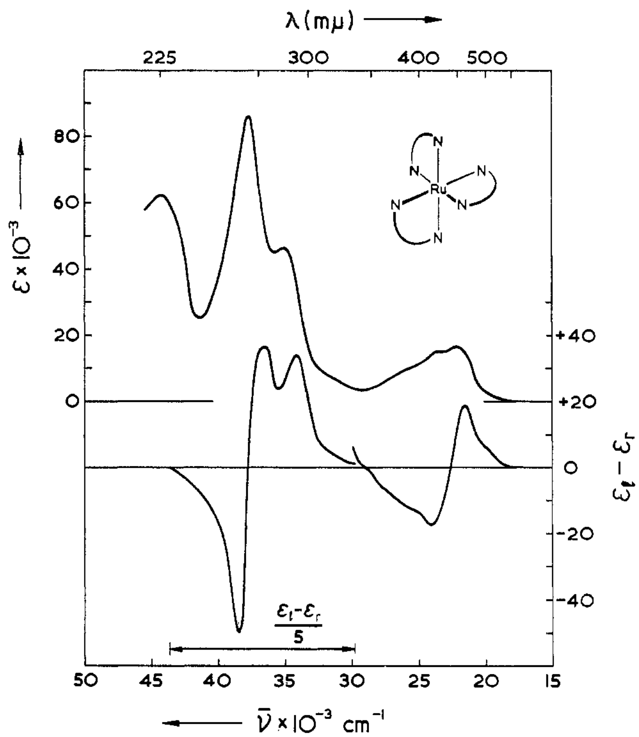

Figure 3.—The absorption and associated circular dichroism spectra of the (+)-[Ru(phen)$_2$bipy](ClO$_4$)$_2$ complex dissolved in water. The figure in the inset represents the predicted absolute configuration of the complex.

The absorption spectrum shows two resolved peaks in this region, one around 38,000 cm^{-1} and one around 35,000 cm^{-1}, which we ascribe to essentially the long-axis polarized $\pi \rightarrow \pi^*$ transitions of the *o*-phenanthroline and 2,2′-bipyridyl ligands, respectively. From the foregoing calculations, we assign the 38,000-cm^{-1} band to the $\Psi_0 \rightarrow \Psi_B{}^+$ transition and the 35,000-cm^{-1} band to the $\Psi_0 \rightarrow \Psi_B{}^-$ transition; the other transition, $\Psi_0 \rightarrow \Psi_A$, which should occur between these two, is not resolved in the absorption spectrum. However, the circular dichroism spectrum reveals the expected three bands which we assign as follows: the positive band around 33,500 cm^{-1} is the $\Psi_0 \rightarrow \Psi_B{}^-$ transition, the positive band around 36,500 cm^{-1} is the $\Psi_0 \rightarrow \Psi_A$ transition, and the negative band around 38,500 cm^{-1} is the $\Psi_0 \rightarrow \Psi_B{}^+$ transition. We therefore conclude that the (+)-Ru(phen)$_2$bipy^{2+} ion has the absolute configuration shown in the inset of Figure 3. The fact that the total area of the two positive peaks is somewhat larger than that of the negative peak is probably due to overlap with the weak circular dichroism arising from the short-axis polarized transitions, which, although they cannot develop exciton circular dichroism, can become optically active in the C_2 field. Furthermore, we have not considered mixing between the long-axis polarized transitions and other transitions of the same symmetry and we have neglected a small term which will give optical activity to the long-axis polarized transitions even in the absence of exciton exchange. The magnitude of this last term can be estimated from the circular dichroism shown by the long-axis polarized transition of the *o*-phenanthroline molecule in, for example, $Co(en)_2phen^{3+}$ (en = ethylenediamine). It has been found[17] to be small compared with the circular dichroism shown by exciton coupling and it is because of this fact that the circular dichroism shown in Figure 3 justifies our use of nondegenerate exciton theory, for, if the *o*-phenanthroline and 2,2′-bipyridyl molecules did not couple in the $Ru(phen)_2bipy^{2-}$ system, we would find two strong (positive and negative) circular dichroism bands[5] under the $\pi \rightarrow \pi^*$ transitions of *o*-phenanthroline and a very weak circular dichroism band under the $\pi \rightarrow \pi^*$ transition of the 2,2′-bipyridyl molecule. Experiment shows that the circular dichroisms exhibited by the long-axis polarized $\pi \rightarrow \pi^*$ transitions of *both* the *o*-phenanthroline and the 2,2′-bipyridyl molecules are exceedingly large and are of comparable magnitudes and therefore justify our initial premises.

III. The Absorption and Circular Dichroism Spectra of the $Ru(bipy)_2phen^{2+}$ Ion

The expressions for the energies, wave functions, dipole strengths, and rotational strengths for the $Ru(bipy)_2phen^{2+}$ ion are identical in all respects with those given in the preceding section for the $Ru(phen)_2bipy^{2+}$ ion except now the numbers 1 and 2 refer to 2,2′-bipyridyl and 3 refers to *o*-phenanthroline in the secular determinant. There is, however, a small observational difference in the ordering of the upper state levels (Figure 2). It is found that the $E_B{}^+$ state lies highest in energy (near the *o*-phenanthroline transition) as before but the states E_A and $E_B{}^-$, totally and mainly associated with the 2,2′-bipyridyl transitions, respectively, both move to lower energies, and it is not immediately obvious, in the present system, which of E_A or $E_B{}^-$ occurs at lower energies. By making a reasonable choice of parameters in the two energy expressions, we find that the energies of the two states are so similar as to suggest that they would not be resolved in the circular dichroism spectrum. This does not, however, present any difficulties in determining the absolute configuration since the two overlapping bands will be of the same sign. For the particular absolute configuration shown in Figure 1, the $\Psi_0 \rightarrow \Psi_B{}^-$ and $\Psi_0 \rightarrow \Psi_A$ transitions should carry positive circular dichroism while the $\Psi_0 \rightarrow \Psi_B{}^+$ transition should carry negative circular dichroism.

In Figure 4 we show the absorption and circular dichroism spectrum of the (+)-$Ru(bipy)_2phen^{2+}$ ion where it will be seen that the predictions of the exciton theory are essentially borne out. The strong, positive circular dichroism band centered around 34,500 cm^{-1} is assigned to the two transitions $\Psi_0 \rightarrow \Psi_A$ and $\Psi_0 \rightarrow \Psi_B{}^-$; the negative band around 38,000 cm^{-1} is assigned to the transition $\Psi_0 \rightarrow \Psi_B{}^+$. A small shoulder on the high-energy (35,000 cm^{-1}) side of the positive band possibly indicates that this two-component transition is partly resolved. The absolute configuration of (+)-$Ru(bipy)_2phen^{2+}$ is therefore the one shown in Figure 4. Again, the sums of the rotational strengths do not vanish and the reasons for this are probably those advanced before. The result, as before, supports the use of nondegenerate exciton theory.

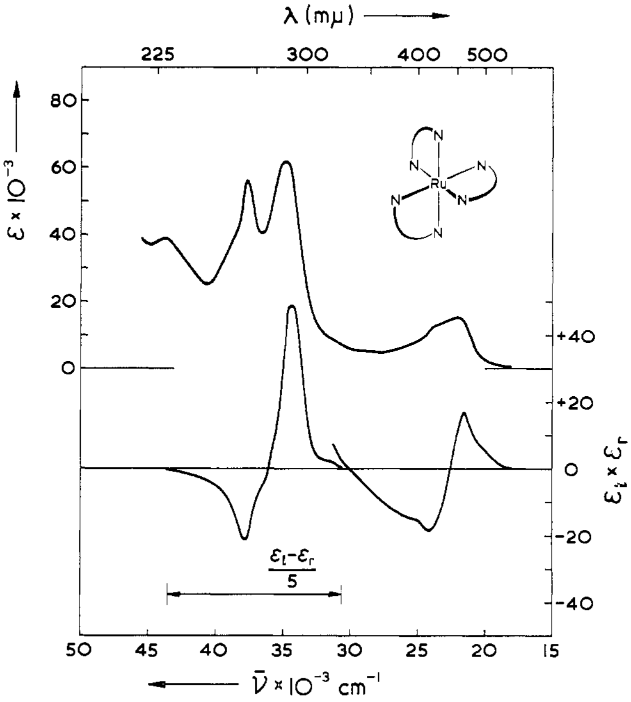

Figure 4.—The absorption and associated circular dichroism spectra of the (+)-$[Ru(bipy)_2phen](ClO_4)_2$ complex in water. The figure in the inset represents the predicted absolute configuration of the complex.

Discussion

The methods used for finding the spectroscopic properties of the two coupled systems (+)-$Ru(phen)_2bipy^{2+}$ and (+)-$Ru(bipy)_2phen^{2+}$ can, of course, be applied to the more common and simpler systems containing only two coupled nonidentical chromophores. For example, it is readily shown for the *cis*-$Ru(phen)(bipy)X_2{}^{n+}$ ion in the absolute configuration related to the one shown in Figure 4, provided the X ligands are "spectroscopically neutral," that the circular dichroism should appear strongly positive under the 2,2′-bipyridyl long-axis polarized $\pi \rightarrow \pi^*$ transition and (equally) strongly negative under the long-axis polarized $\pi \rightarrow \pi^*$ transition of the *o*-phenanthroline molecule. We chose the more complicated systems because they provided us with the possibility of distinguishing between the distinctly different predictions emanating from the use of either degenerate or nondegenerate theory. In the particular examples described here, experiment clearly shows that a more complete description of the exciton circular dichroism is given by the use of the nondegenerate method.

There is, however, no difference in principle between the two methods, and, in many ways, we may regard the degenerate problem as a special case of the more general nondegenerate problem. Thus, by making the appropriate substitutions in the equations given here, it is readily shown that in the present two systems, when all three ligands become the same, the three eigenvalues become $\Delta E_1 + 2V_{12}$, $\Delta E_2 - V_{12}$, and $\Delta E_3 - V_{12}$, and the corresponding eigenfunctions are $(1/\sqrt{3})(-\Phi_1 - \Phi_2 - \Phi_3)$, $(1/\sqrt{6})(-2\Phi_3 + \Phi_2 + \Phi_1)$, and $(1/\sqrt{2})\cdot(\Phi_1 - \Phi_2)$, respectively. These are precisely the eigenvalues and eigenfunctions obtained for the D_3 system with three identical chromophores; *i.e.*, when $\Delta E_1 = \Delta E_2 = \Delta E_3$, $\Phi_1 = \Phi_2 = \Phi_3$ and $V_{12} = V_{13} = V_{23}$. This result is quite general. Furthermore, the equations are also applicable to C_2 systems containing only two identical chromophores, *e.g.*, the *cis*-$\mathrm{Ru(phen)_2X_2}^{2+}$ ion, for, if ΔE_3 and V_{13} are set to zero in the eigenvalues, the energies become $\Delta E_1 - V_{12}$ and $\Delta E_1 + V_{12}$ and the corresponding eigenfunctions are $(1/\sqrt{2})(\chi_1'\chi_2 - \chi_1\chi_2')$ and $(1/\sqrt{2})(\chi_1'\chi_2 + \chi_1\chi_2')$, respectively. These, of course, are the energies and functions apposite for C_2 systems.[5] For systems containing more than two nonidentical chromophores, the computational difficulties rapidly increase with the number of nonidentical chromophores and analytic solutions are not generally possible.

The complex ions $\mathrm{Ru(phen)_2bipy}^{2+}$ and $\mathrm{Ru(bipy)_2phen}^{2+}$ were prepared by treating $\mathrm{Ru(phen)_2Cl_2}$[18] and $\mathrm{Ru(bipy)_2Cl_2}$[19,20] with 2,2′-bipyridyl and *o*-phenanthroline, respectively. They were resolved through their antimonyl (+)-tartrate salts. The least soluble diastereoisomers contained the $\mathrm{Ru(phen)_2bipy}^{2+}$ and $\mathrm{Ru(bipy)_2phen}^{2+}$ ions of the same absolute configurations. Coordination compounds formed between the divalent ruthenium ion and the *o*-phenanthroline and 2,2′-bipyridyl molecules are extremely stable and not prone to disproportionation.[18–24] Therefore, the likelihood that the $\mathrm{Ru(phen)_3}^{2+}$ and $\mathrm{Ru(bipy)_3}^{2+}$ ions are formed during reaction is precluded. This is confirmed by an examination of the absorption and circular dichroism spectra which are consistent with those expected for the $\mathrm{Ru(phen)_2bipy}^{2+}$ and $\mathrm{Ru(bipy)_2phen}^{2+}$ ions, and the possibility that these are composite spectra resulting from various proportions of the $\mathrm{Ru(phen)_3}^{2+}$ and $\mathrm{Ru(bipy)_3}^{2+}$ ions is excluded. No racemization of either ion was detected after aqueous solutions were allowed to stand at room temperature for 1 week. In both cases the racemic perchlorate salts are less soluble in water than the corresponding active salts.

Experimental Section

The Preparation and Resolution of the $\mathbf{Ru(phen)_2bipy}^{2+}$ Ion.—$\mathrm{Ru(phen)_2Cl_2}$[18] (1 g) was suspended in water (200 ml) and ethanol (200 ml) and the mixture was boiled until all of the chloro complex had dissolved (~2 hr). 2,2′-Bipyridyl (0.31 g) was added to this resulting brown solution, and, after boiling for a further 2 hr, the now bright orange reaction mixture was filtered and evaporated to dryness on a steam bath. The dark brown residue was taken up in a warm solution of methanol and ethanol (15 ml, 50%) and carefully precipitated with ether. The $\mathrm{[Ru(phen)_2bipy]Cl_2}$ complex came down as a fine yellow powder which was collected and washed with ether.

Sodium antimonyl (+)-tartrate (0.7 g) in water (10 ml) was added to the $\mathrm{[Ru(phen)_2bipy]Cl_2}$ salt (1.2 g) in water (25 ml) at 50°. On scratching the sides of the vessel, bright orange-red needles of the diastereoisomer began to precipitate, and, after the mixture was allowed to cool at room temperature, the crystals (1.1 g) were collected and washed with water (10 ml) followed by acetone. Upon the addition of a few drops of 0.5 *M* aqueous lithium perchlorate solution to the aqueous filtrate, a red gum deposited which was filtered, and the resulting clear orange filtrate was brought to 80° and lithium perchlorate was added until the solution became cloudy. After *slowly* cooling the solution to 5°, the red-orange needles were collected, washed with ice water, followed by acetone–ether (20% acetone), and finally with ether. The complex was recrystallized from warm water by the addition of dilute perchloric acid; $[\alpha]_D$ −1120°, 0.5% solution in water, 10-cm tube, α_D −0.56°. *Anal.* Calcd for $\mathrm{[Ru(phen)_2bipy](ClO_4)_2\cdot 2H_2O}$ ($\mathrm{RuC_{34}H_{28}O_{10}Cl_2}$): C, 47.9; H, 3.3; N, 9.9. Found: C, 47.8; H, 3.0; N, 10.2.

The recrystallized (from boiling water ~500 ml) diastereoisomer was ground with perchloric acid (10 ml, concentrated), filtered, and washed with hot water (25 ml). The residue was similarly treated with a further 10 ml of concentrated perchloric acid, filtered, and extracted on the filter with hot water until the washings became colorless. After the addition of perchloric acid to the combined filtrates, the fine orange-red needles thus formed were collected and recrystallized and washed by the same methods as described for the other isomer; $[\alpha]_D$ +1120°, 0.05% solution in water, 10-cm tube, α_D +0.56°. *Anal.* Calcd for $\mathrm{[Ru(phen)_2bipy](ClO_4)_2\cdot 2H_2O}$ ($\mathrm{RuC_{34}H_{28}N_6O_{10}Cl_2}$): C, 47.9; H, 3.3; N, 9.9. Found: C, 47.9; H, 3.0; N, 9.8.

Preparation and Resolution of the $\mathbf{Ru(bipy)_2phen}^{2+}$ Ion.—A suspension of $\mathrm{Ru(bipy)_2Cl_2}$[19,20] (1.22 g) in water (200 ml) and methanol (100 ml) was heated until dissolution was complete whereafter *o*-phenanthroline monohydrate (0.5 g) was added to the solution which was then refluxed for 1 hr. The resulting bright orange solution was filtered and evaporated to dryness on a steam bath. After the resulting dark brown residue was taken up in hot methanol (20 ml), the $\mathrm{[Ru(bipy)_2phen]Cl_2}$ salt came down as a fine yellow powder upon the careful addition of ether. It was collected and washed with ether.

Sodium antimony (+)-tartrate (2 g) in water (10 ml) was added to a warm solution of the $\mathrm{[Ru(bipy)_2phen]Cl_2}$ salt (1.2 g) in water (30 ml). Scratching the walls of the flask induced the diastereoisomer to precipitate as fine golden needles which, after the solution was held at 5° for 1 hr, were collected and washed with a minimum of ice water followed by acetone. The diastereoisomer was dissolved in hot water (100 ml) and the (+)-$\mathrm{[Ru(bipy)_2phen](ClO_4)_2}$ was precipitated by the addition of perchloric acid. After the solution was allowed to cool to room temperature, the fine orange-red crystals were collected and washed with water followed by acetone in ether (20% acetone). The salt was recrystallized from water by the addition of perchloric acid; $[\alpha]_D$ +1040°, 0.025% solution in water, 10-cm tube, α_D +0.26°. *Anal.* Calcd for $\mathrm{[Ru(bipy)_2phen](ClO_4)_2\cdot 2H_2O}$ ($\mathrm{RuC_{32}H_{28}N_6O_{10}Cl_2}$): C, 46.3; H, 3.4; N, 10.1. Found: C, 46.6; H, 3.1; N, 10.3.

Dilute perchloric acid was added dropwise to the filtrate obtained from the isolation of the diastereoisomer. The first crop of crystals obtained was optically inactive; these were filtered

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off and more perchloric acid was added to the resulting filtrate. By this method the complex was fractionally crystallized and the final fraction had the highest rotation. It was collected and washed as before; $[\alpha]_{\text{D}}$ −320°, 0.025% solution in water, 10-cm tube, α_{D} −0.08°. *Anal.* Calcd for $[Ru(bipy)_2phen](ClO_4)_2 \cdot 2H_2O$ ($RuC_{32}H_{28}N_6O_{10}Cl_2$): C, 46.3; H, 3.4; N, 10.1. Found: C, 46.7; H, 3.1; N, 10.4.

The diastereoisomer obtained from the $Ru(bipy)_2phen^{2+}$ ion is much more soluble in water than that obtained from the $Ru(phen)_2bipy^{2+}$ ion, and it is probable that, with larger amounts of the $[Ru(bipy)_2phen]Cl_2$ salt and smaller volumes of water, the (−)-$Ru(bipy)_2phen^{2+}$ ion could be obtained optically pure in convenient amounts. However, the two (+) isomers used for the circular dichroism studies are probably optically pure.

The absorption spectra were measured using a Unicam SP-800-B (recording) spectrophotometer and the circular dichroism spectra were obtained using a Roussel-Jouan Dichrographe (sensitivity 1.5 × 10^{-4}).

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Nuclear Magnetic Resonance Determination of the Absolute Configuration of Complexes of Cobalt(III) with Asymmetric Tetradentate Ligands[1a]

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The preparation, separation, and characterization of a series of cobalt(III) complexes containing the asymmetric tetradentate ligand ethylenediamine-N,N′-di-L-α-propionate (LL-EDDP) or -D-α-propionate (DD-EDDP) and ethylenediamine (en) or *l*-propylenediamine (*l*-pn) are reported. The absolute configurations of the complexes are assigned by considering the proton nmr spectra and the known configuration of the ligand. The L-*trans*-LL-EDDP isomer with the methyl group pointed toward the en exhibits a complicated en signal due to steric interaction. The acetate proton pattern confirms that the proton points toward the tetradentate backbone. In the D-*trans* isomer the methyl group points toward the backbone and a single en peak is observed plus an acetate proton pattern consistent with the proton pointing toward the en. Similar results were obtained for the other complexes. ORD and CD data confirm the nmr assignments.

Introduction

The study of the stereochemistry of the octahedral complexes of cobalt(III) has been the object of a large number of investigations during the past half-century.[2] In only a small minority of these cases, however, has an optically active ligand been utilized to influence the stereochemistry. Complexes containing optically active diamines and α-aminocarboxylic acids have been extensively studied.[2] However, few complexes with optically active multidentate chelating agents are known. The stereochemistry with optically active analogs of the tetradentate ligand triethylenetetramine has been studied. Asperger and Liu[3] utilized optically active L,L-2,9-diamino-4,7-diazadecane and observed stereospecific formation of only the D-α-*cis* and L-β-*cis* optical isomers as determined by the ligand stereochemistry. Worrell and Busch[4] prepared complexes from racemic 4-methyl-1,8-diamino-3,6-dithiaoctane and obtained the α-*cis* and β-*cis* complexes as racemates. Gill[5] described the linear hexadentate ligand 3,10-bis-(salicylideneamino)-5,8-dithiadodecane but did not investigate the isomerism of its metal complexes. Dwyer and MacDermott[6] obtained only the isomers D-(−) and L-(+) upon the reaction of racemic 4-methyl-1,8-bis(salicylideneamino)-3,6-dithiaoctane although three apparently uncrowded and strain-free forms exist for each isomer of the base. Utilizing optically active ligand, 85% D-(−) and 15% L-(−) were obtained. Complexes prepared with optically active analogs of EDTA coordinate stereospecifically as found by Dwyer and Garvan[7] with complexes of propylenediaminetetraacetic acid and *trans*-1,2-cyclohexanediaminetetraacetic acid. Legg and Cooke[8] have shown that the steric requirements of D-(or L-)aspartate (aspart), functioning as a tridentate ligand, dictate the formation of both geometric and optical isomers in the complex Co(D- or L-aspart)(dien)⁺.

The preparation, separation, and characterization of a series of cobalt(III) complexes containing the asymmetric tetradentate ligand ethylenediamine-N,N′-di-L-α-propionate (LL-EDDP) or -D-α-propionate (DD-EDDP) are reported in this paper. The ligands were prepared by allowing optically active alanine of known configuration to react with 1,2-dibromoethane. Complexes containing ethylenediamine or propylenedi-

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(1) (a)Abstracted in part from the Ph.D. thesis of L. N. Schoenberg, The University of Michigan, 1966. (b) Author to whom correspondence should be addressed at the Department of Chemistry, Western Michigan University, Kalamazoo, Mich.

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