TABLE I
RELATIVE RATES FOR TRIBUTYLTIN HYDRIDE–BIS(DIMETHYLAMINO)CHLOROBORANE REACTION

| Conditions | Relative rate[a] | Std dev |
|---|---|---|
| Neat reactants | 1.00 | 0.2 |
| Added AIBN[b] | 0.96 | 0.3 |
| Added galvinoxyl[b] | 1.56 | 0.2 |
| Chlorobenzene solvent[c] | 0.67 | 0.1 |
| Hexane solvent[c] | 0.04 | 0.01 |

[a] Slope of least-squares straight line for plot of B–H/Sn–H ratio *vs.* time, normalized to 1.00 for the neat reactants. [b] Additive at 10 mole % level. [c] Solvent:solute mole ratio = 20:1.

intermediate or transition state has been demonstrated for the reduction of trichloroborane with an optically active silicon hydride.[5] A similar configuration, with some charge separation to explain solvent effects, seems likely here. However, a direct displacement mechanism cannot be ruled out by the data at hand.

## Experimental Section

**Bis(dimethylamino)borane** (1).—A mixture of freshly distilled bis(dimethylamino)chloroborane (6.15 g, 0.0457 mol) and 13.30 g (0.0457 mol) of tributyltin hydride was heated 0.5 hr at 90°. The pot temperature then was raised and 0.7 g of distillate was removed, bp 69–71°. After standing over the weekend, distillation was continued to give a second fraction, 3.35 g, bp 68° (52 mm). The product, obtained in 73% yield, was identified as bis(dimethylamino)borane by comparison of boiling point (lit.[6] bp 70° at 52 mm, extrapolated) and by an identical infrared spectrum with that of an authentic sample. The residue showed infrared peaks characteristic of tributyltin chloride plus additional absorptions at 1525, 1510, 1350 (w), 1220, 1190 (w), 1110, 905 (w), and 807 (w) cm$^{-1}$.

**Relative Rates.**—Bis(dimethylamino)chloroborane (2.0 g, 0.0149 mol) was dissolved in 3.8 ml (4.0 g, 0.0149 mol) of tributyltin hydride in a three-necked flask with a rubber septum and a reflux condenser topped with a nitrogen by-pass. At time zero, the flask was immersed in a bath at 60.5 ± 0.5°. At noted intervals, samples were removed by a hypodermic needle through the rubber septum and their infrared spectra were recorded. Extent of reaction was followed by the increasing ratio of B–H absorption at 2480 cm$^{-1}$ to Sn–H absorption at 1820 cm$^{-1}$. Separate runs were made with the above quantities of reactants in the presence of the following additives: (A) $\alpha,\alpha'$-azobis(isobutyronitrile), 0.049 g, 0.0015 mol; (B) galvinoxyl, 0.124 g, 0.0015 mol; (C) hexane, 25.6 g, 0.298 mol; (D) chlorobenzene, 33.5 g, 0.298 mol. Relative rates were obtained by comparing the slopes of plots of B–H/Sn–H ratios *vs.* time.

**1,3,2-Benzodioxaborolane** (2).—A solution of 2-chloro-1,3,2-benzodioxaborole (4.9 g, 0.0318 mol) and tributyltin hydride (8.06 g, 0.0318 mol) was heated at 90° 2 hr and allowed to stand at room temperature overnight. Distillation of the reaction mixture provided 1.59 g (42% yield) of 2 at 88° (156 mm); infrared $\nu_{\max}^{\mathrm{B-H}}$ 2680 cm$^{-1}$.

*Anal.* Calcd for $C_6H_5BO_2$: C, 60.07; H, 4.21; B, 9.03. Found: C, 59.89; H, 4.18; B, 8.99.

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(5) C. J. Attridge, R. N. Hazeldine, and M. J. Newlands, *Chem. Commun.*, **24**, 911 (1966).

(6) G. E. Coates, *J. Chem. Soc.*, 3481 (1950).

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# The Absolute Configurations of Bis-Bidentate Chelate Compounds. The Case of the *cis*-Bis(pyridine)bis(*o*-phenanthroline)-ruthenium(II) ion

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The present methods of determining the absolute configurations of dissymmetric metal complexes by means of their circular dichroism spectra are of two kinds, namely, the empirical and nonempirical. In the former, the absolute configurations of a series of related complexes are determined by a knowledge of the absolute configuration of one complex[1,2] or that of the ligand[3,4] together with the sign of the circular dichroism exhibited by equivalent[2,4] spectroscopic transitions. The nonempirical method, however, requires only a knowledge of the polarization directions of particular electronic transitions of the molecule and, in principle, gives the absolute configuration of the molecule without reference to or a knowledge of the independently determined absolute configuration of a related molecule. This latter method was first proposed classically by Kuhn,[5] set in a quantum mechanical framework by Moffitt,[6] and applied to and developed for inorganic complexes by Mason.[7-9] The predictions of the nonempirical method have been recently confirmed by the X-ray diffraction determination[10] of the absolute configuration of the (−)-tris(*o*-phenanthroline)iron(II) ion, (−)-$[Fe(phen)_3]^{2+}$. In this note we wish to outline the method for determining the absolute configurations of *cis*-bis-bidentate complexes containing conjugated bidentate ligands. For this purpose we have chosen the recently resolved[11] *cis*-bis(pyridine)bis(*o*-phenanthroline)ruthenium(II) ion, *cis*-$[Ru(phen)_2(py)_2]^{2+}$, which may serve as a representative example of this class of complexes.

The $\pi \rightarrow \pi^*$ transitions of the *o*-phenanthroline molecule are either short-axis ($z$) or long-axis ($x$) polarized (see Figure 1(a)). These transitions, however, have not been rigorously identified, although molecular orbital calculations, together with the polarized crystal

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(1) J. P. Mathieu, *Bull. Soc. Chim. France*, **3**, 463, 476 (1936).

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

(3) E. J. Corey and J. C. Bailar, *J. Am. Chem. Soc.*, **81**, 2620 (1959).

(4) B. Bosnich, *Proc. Roy. Soc.* (London), **A297**, 88 (1967).

(5) W. Kuhn, *Z. Physik. Chem.*, **B4**, 14 (1929).

(6) W. Moffitt, *J. Chem. Phys.*, **25**, 467 (1956).

(7) A. J. McCaffery and S. F. Mason, *Proc. Chem. Soc.*, 211 (1963).

(8) E. Larsen, S. F. Mason, and G. H. Searle, *Acta Chem. Scand.*, **20**, 191 (1966).

(9) S. F. Mason and B. J. Norman, *Inorg. Nucl. Chem. Letters*, **3**, 285 (1967).

(10) D. H. Templeton, A. Zalkin, and T. Ueki, *Acta Cryst.*, **21**, A154 (supplement) (1966).

(11) B. Bosnich and F. P. Dwyer, *Australian J. Chem.*, **19**, 2229 (1966).

spectrum of phenanthrene,[12–14] leave little doubt that the intense band at around 38,000 cm$^{-1}$ of *o*-phenanthroline is long-axis polarized and that the lower energy transitions are short-axis polarized. Upon complex formation these transitions remain largely unmodified,[15] except that the individual electric transition dipole moments of the ligands can couple to produce exciton splittings. In *cis*-bis-*o*-phenanthroline complexes the short-axis polarized transitions couple to give only electric dipole transition moments in the zero order, but the long-axis polarized transitions give rise to parallel electric and magnetic dipole transition moments which therefore, in a classical sense, give rise to helical displacements of charge which produce the exciton optical activity. It is this zero-order rotational strength produced by the long-axis polarized transitions of *o*-phenanthroline which concerns us here.

The *cis*-$[\mathrm{Ru(phen)_2(py)_2}]^{2+}$ ion belongs to the point group $C_2$ and the two coupling modes of the long-axis polarized transitions of *o*-phenanthroline transform according to the irreducible representations A and B. The totally symmetric ground-state function $\Psi_0$ may be written as $\Psi_0 = \varphi_1\varphi_2$, where the functions $\varphi_1$ and $\varphi_2$ refer to ground states of molecules 1 and 2, respectively. Similarly, the excited-state functions referring to the long-axis polarized transition are written as

$$\Phi_1 = \varphi_1'\varphi_2$$

$$\Phi_2 = \varphi_1\varphi_2'$$

where the primes represent the excited-state functions. These last two functions may be combined to form the two wave functions for the two coupling modes

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

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

Transitions from the ground-state function $\Psi_0$ to the excited-state wave function $\Psi_A$ are *z*-axis polarized while excitations to $\Psi_B$ are *x,y* polarized. These two coupling modes are shown pictorially in Figure 1. For the particular absolute configuration of the molecule shown in Figure 2, the dipole strength, $D_z$, and the rotational strength, $R_z$, in the *z* direction for the transition $\Psi_0 \rightarrow \Psi_A$ are given by

$$D_z = \frac{1}{2}p^2$$

$$R_z = -\sqrt{\frac{2}{3}}\pi\bar{\nu}rp^2$$

where $p$ is the electric transition moment which gives the observable dipole strength at a wave number frequency of $\bar{\nu}$ in the individual *o*-phenanthroline molecule, and $r$ is the half-distance (radius) between the "centers" of the electric transition moments of the two molecules. Similarly, the dipole strength, $D_{xy}$, and the rotational strength, $R_{xy}$, in the *x,y* directions for the transition $\Psi_0 \rightarrow \Psi_B$ are given by

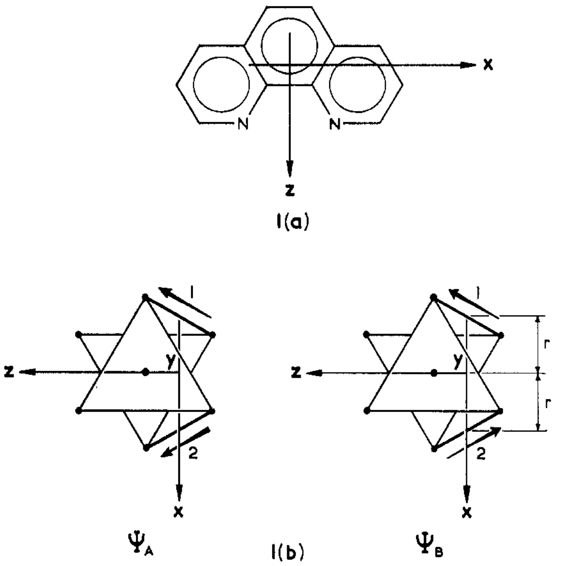

Figure 1.—The short (*z*) and long (*x*) axes of the *o*-phenanthroline molecule are shown in 1(a). In 1(b) the *z*-polarized $\Psi_A$ coupling mode is shown on the left and the *x,y*-polarized $\Psi_B$ coupling mode is shown on the right. In all cases the *y* axis projects normal to the paper.

$$D_{xy} = \frac{3}{2}p^2$$

$$R_{xy} = +\sqrt{\frac{2}{3}}\pi\bar{\nu}rp^2$$

Were these two transitions of the same energy, the rotational strengths would vanish and the dipole strength would equal twice that of an individual complexed *o*-phenanthroline molecule (see equations). The situation is more interesting than this, however, since the dipole–dipole interactions of the two modes are different. Using the point dipole–point dipole approximation,[16] the $\Psi_A$ coupling mode will appear at lower energies by a factor of $-p^2/4R^3$ and the $\Psi_B$ coupling mode will appear at higher energies by a factor of $+p^2/4R^3$ relative, approximately, to the energy of the transition of the isolated complexed *o*-phenanthroline molecule. $R$ is the distance between the "centers" of the excitation moments of the two complexed *o*-phenanthroline molecules.

Thus the exciton theory of optical activity predicts that, in the region of the long-axis polarized transition of *o*-phenanthroline complexed in the absolute configuration shown in Figure 2, the circular dichroism should appear strongly negative at lower energies and (equally) strongly positive at higher energies. The lower energy transition ($\Psi_0 \rightarrow \Psi_A$) involves a left-handed helical displacement of charge along and about the *z* axis. The higher energy transition $\Psi_0 \rightarrow \Psi_B$ involves, in the axis frame chosen in Figure 1, a right-handed helical displacement of charge along and about

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[12] D. S. McClure, *J. Chem. Phys.*, **25**, 481 (1956).

[13] T. Azumi and S. McGlynn, *ibid.*, **37**, 2413 (1962).

[14] D. P. Craig and R. D. Gorden, *Proc. Roy. Soc.* (London), **A288**, 69 (1965).

[15] J. Hidaka and B. E. Douglas, *Inorg. Chem.*, **3**, 1180 (1964).

[16] E. G. McRae and M. Kasha, "Physical Processes in Radiation Biology," Academic Press Inc., New York, N. Y., 1964, p 23.

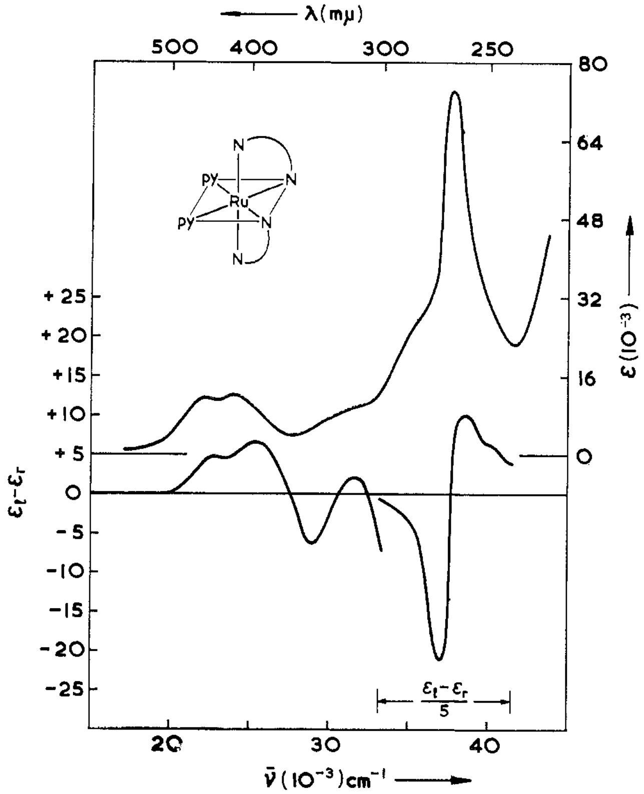

Figure 2.—The absorption spectrum and associated circular dichroism of a methanol solution of *cis*-$[Ru(phen)_2(py)_2](ClO_4)_2$ which has the absolute configuration shown in the inset.

the *y* axis.[17] The isomer with the opposite absolute configuration to the one in Figure 2 will have the bands in the same positions, but the lower energy band will be positive and the higher energy band will be negative.

The absorption spectrum and the associated circular dichroism of a methanol solution of (−)-*cis*-$[Ru(phen)_2(py)_2](ClO_4)_2$ are shown in Figure 2. In the energy region between about 18,000 and 35,000 $cm^{-1}$ the relatively weak circular dichroism under the moderately strong absorption bands arises from two main sources. Transitions occurring between about 18,000 and 28,000 $cm^{-1}$ most probably involve the excitation of the electrons from filled d orbitals of the metal to the empty $\pi^*$ orbitals of the *o*-phenanthroline ligands. We wish here to make only two remarks about these transitions; first, unlike the active $[Ru(phen)_3]^{2+}$ ion[7] the circular dichroism is of the same sign throughout this region, and, second, the supposition that these are charge-transfer bands is supported by their intensities and the fact that they vary in energy position upon substitution of the pyridine ligands.[18] Transitions occurring in the region 28,000–35,000 $cm^{-1}$ are short-axis polarized transitions of the *o*-phenanthroline ligand and they do not vary greatly in position or intensity upon substitution of the pyridine ligands. These transitions cannot develop exciton circular dichroism but can, in principle, become optically active by mixing with other transitions in the presence of the $C_2$ field. They should show, as is observed, relatively weak circular dichroism compared to the long-axis polarized transitions. Under the long-axis polarized band at around 38,000 $cm^{-1}$ the circular dichroism is at low energies strongly negative and at higher energies strongly positive in conformity with the predictions of the exciton theory. The fact that the higher energy positive band is weaker than its negative counterpart is due, probably, to instrumental insensitivity in this region and to the fact that the present approximate theory does not take into account the possibility of mixing between these two bands and other transitions of the system. The exciton theory also predicts that the intensity of the ordinary absorption associated with the lower energy negative circular dichroism band should be three times weaker than the absorption band associated with the higher energy positive circular dichroism. An inspection of Figure 2 will reveal that this expectation is apparently borne out.[19] We therefore conclude that the absolute configuration of the optical isomer of *cis*-$[Ru(phen)_2(py)_2]^{2+}$ showing the circular dichroism in Figure 2 has the absolute configuration shown in the inset of Figure 2. The monosubstituted complexes[11] of the type *cis*-$[Ru(phen)_2(py)X]^{n+}$, where X = $Cl^-$, $Br^-$, $I^-$, $NO_2^-$, $NCS^-$, $CN^-$, $N_3^-$, or $H_2O$, prepared from this optical isomer of *cis*-$[Ru(phen)_2(py)_2]^{2+}$ all show circular dichroism spectra which are almost identical with that shown in Figure 2, and therefore they all have the absolute configuration depicted in the inset of Figure 2.

The arguments that have been employed here also apply to, for example, the *cis*-bis-bidentate complexes of 2,2′-bipyridyl and the acetylacetonate ion. For the absolute configuration shown in Figure 2, these complexes should show strong negative circular dichroism at lower energies and equally strong positive circular dichroism at higher energies in the regions of the long-axis polarized transitions of the ligands. For the 2,2′-bipyridyl molecule the long-axis polarized transition should occur at 34,000 $cm^{-1}$ and at around 35,000 $cm^{-1}$ for the acetylacetonate ion.[8] When the two chromophores are not degenerate, as in, for example, complexes of the type *cis*-$[M(phen)(bipy)X_2]^{n+}$, the situation, although sometimes tractable, is less simple. We hope to report on these systems shortly.

### Experimental Section

The complexes *cis*-$[Ru(phen)_2(py)X]^{n+}$, where X = $Cl^-$, $Br^-$, $I^-$, $N_3^-$, $NO_2^-$, $NCS^-$, $CN^-$, or py, were prepared, purified, and resolved by methods described elsewhere.[11] The absorption spectra were measured using a Unicam SP 800B recording spectrophotometer and the circular dichroism spectra were obtained using a Roussel–Jouan Dichrographe (sensitivity 1.5 × $10^{-4}$).

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(17) It is worth noting that if we choose the axis frame shown in Figure 1, all of the transition magnetic moment of the $\Psi_0 \rightarrow \Psi_B$ transition is "concentrated" along the *y* axis (and none along the *x* axis) whereas the transition electric dipole moment has components along both *x* and *y* directions. However, the *x* and *y* axes are not uniquely defined in the point group $C_2$ and this observation is only of methodological interest, although it applies generally to $C_2$ systems.

(18) B. Bosnich and F. P. Dwyer, *Australian J. Chem.*, **19**, 2235 (1966).

(19) However, when extensive overlap of bands occurs, this intensity argument is not always useful and can be misleading. Indeed, the conclusions[7] about the absolute configuration of (−)-$[Ru(phen)_3]^{2+}$ were based on this intensity argument and led to the wrong conclusion as to the absolute configuration of this molecule. This error was subsequently corrected[9] by basing the arguments on the splitting directions which are reliable.