Optical Rotatory Power of Co-ordination Compounds. Part XIII.[1] Circular Dichroism of Hetero-trischelated Metal Complexes of Bipyridyl and Phenanthroline

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Absorption and circular dichroism spectra are reported for the hetero-trischelated complexes [M phen$_2$bipy]$^{n+}$ and [M bipy$_2$phen]$^{n+}$ of nickel(II) and osmium-(II) and -(III) (bipy = 2,2'-bipyridyl and phen = 1,10-phenanthroline). The exciton theory of optical activity is developed for the hetero-trischelated complexes with two-fold rotational symmetry, and it is found that the relative rotational strengths and frequencies of the circular dichroism bands of the complexes studied in the 30,000—40,000 cm.$^{-1}$ region are in satisfactory agreement with the model. The dipole strengths of the isotropic absorption of the complexes show less satisfactory agreement with the theory, and the discrepancies are attributed to a minor contribution to the absorption from excitations of a charge-transfer and internal ligand origin which are polarised along the short in-plane axis of the ligand. These excitations do not contribute to the optical activity which derives principally from long-axis polarised ligand transitions. The (+)-isomers of the complexes studied are found to have the same configuration $P(C_2)$, as that of (−)-[Fe phen$_3$]$^{2+}$ established by X-ray crystallography.

IN the preceding paper [1] it is shown that the circular dichroism of tris-phenanthroline (phen) and -bipyridyl (bipy) complexes of the iron-group metal ions arises primarily from exciton interaction between the ligand transition moments which are long-axis polarised and degenerate in the zero order. A small fraction of the rotational strength due to the ligand excitations in the u.v. region is borrowed by the charge-transfer transitions of the complex in the visible region, and interligand and metal–ligand bonding modify the frequencies of the ligand circular dichroism bands in the u.v., but none of these effects negate the main conclusions of the exciton theory.[1] In the corresponding complexes of other metal ions interligand bonding is more significant only if the distance between adjacent nitrogen atoms of different ligands is appreciably <2·79 Å, the value [2] for [Fe phen$_3$]$^{2+}$, and metal–ligand π-bonding is expected to be generally of less significance. The degree of metal–ligand π-bonding is approximately proportional to the intensity of the metal–ligand charge-transfer bands, which is large for the tris-phenanthroline and -bipyridyl complexes of the iron-group metal ions,[1] so that degenerate exciton theory should be applicable with less qualification to the corresponding complexes of metal ions which give only weak or moderate charge-transfer bands, notably, nickel(II),[3,4] cobalt(III),[5,6] and chromium(III).[5]

If the symmetry of a trischelated complex is reduced from D_3 to C_2, by replacing one of the bidentate ligands with another of a different type, the requirements of the exciton theory of optical activity are diversified, permitting a more detailed comparison of the theory with experiment.[7,8] In a hetero-trischelated complex with C_2 symmetry the exciton modes which are doubly degenerate in the analogous homo-trischelated D_3 complex are split and give rise in principle to distinct circular dichroism bands. Thus the ligand transitions with long-

axis polarisation produce three circular dichroism bands with determinate areas and frequencies in hetero-trischelated complexes if the frequency separation be-

(I)

(II)
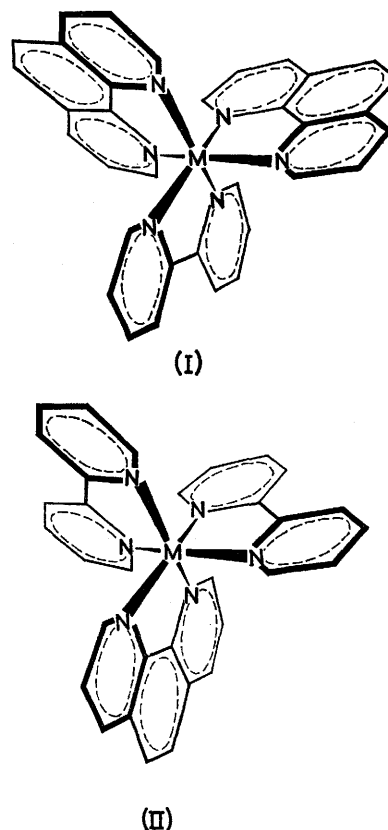
tween the excitations of the dissimilar ligands is not too large, whereas the corresponding excitations in homo-

[1] Part XII, A. F. McCaffery, S. F. Mason, and B. F. Norman, preceding paper.

[2] D. H. Templeton, A. Zalkin, and T. Ueki, *Acta Cryst., Suppl.,* 1966, **21**, *A,* 154.

[3] F. P. Dwyer and E. C. Gyarfas, *J. Proc. Roy. Soc. New South Wales,* 1949, **83**, 232.

[4] J. Hidaka and B. Douglas, *Inorg. Chem.,* 1964, **3**, 1180.

[5] C. S. Lee, E. M. Gorton, H. M. Neumann, and H. R. Hunt, jun., *Inorg. Chem.,* 1966, **5**, 1397.

[6] S. F. Mason and B. J. Norman, *Inorg. Nuclear Chem. Letters,* 1967, **3**, 285.

[7] S. F. Mason and B. J. Norman, *Chem. Phys. Letters,* 1968, **2**, 22.

[8] B. Bosnich, *Inorg. Chem.,* 1968, **7**, 2379.

trischelated complexes with D_3 or C_3 symmetry, or in homo- or hetero-bichelated complexes with C_2 or C_1 symmetry, respectively, give rise to only two dichroism bands.

The p-bands of phenanthroline and bipyridyl at 37,800 and 35,600 cm.$^{-1}$, respectively, are predominantly long-

a ground-state and an excited-state electronic wave-function, ϕ and ϕ', respectively, the ground state of the complex is represented by the simple product function,

$$\psi_0(A) = \phi_a\phi_b\phi_c \qquad (1)$$

and three excited-states of the complex ion are formed

The frequencies, $\bar{\nu}$ (10^3 cm.$^{-1}$), dipole strengths, D (10^{-36} c.g.s.), and rotational strengths R (10^{-38} c.g.s.), of the exciton transition arising from the long-axis polarised excitations giving the p-band of the ligands in [M phen$_2$bipy]$^{n+}$ (I) and [M bipy$_2$phen]$^{n+}$ (II). Theoretical values of the rotational strengths refer to the isomers with the configurations (I) and (II), respectively

Isomer	$R_2(B)$	$R(A)$	$R_1(B)$	$\bar{\nu}_2(B)$	$\bar{\nu}(A)$	$\bar{\nu}_1(B)$	$D_2(B)$	$D(A)$	$D_1(B)$	Ref.
Calc. (I)	+1·2	+6·0	−7·2	35·2	37·1	38·9	11	15	48	
(+)$_D$-[Ni phen$_2$bipy]$^{2+}$	+1·5	+3·0	−3·8	33·8	36·5	38·2	21	54		(9)
(+)$_{546}$-[Os phen$_2$(bipy)]$^{2+}$	+1·8	+2·9	−4·7	34·5	37·2	38·8	30	58		(10)
(+)$_{546}$-[Os phen$_2$bipy]$^{3+}$	+0·5	+1·5	−1·9	32·2	35·8	38·1	19	57		(10)
Calc. (II)	−3·4	+2·6	+0·8	38·6	35·6	35·8	40	11	7	
(+)$_{546}$-[Os bipy$_2$phen]$^{2+}$	−1·7	+1·9	+0·5	37·9	34·1	35·5	35	42		(10)
(+)$_{546}$-[Os bipy$_2$phen]$^{3+}$	−1·5	+1·1	+0·7	37·7	31·8	33·1	40	28		(10)

axis polarised,[1] and the frequency interval between them is small, so that the hetero-trischelated complexes,[8-10] [M phen$_2$bipy]$^{n+}$ (I) and [M bipy$_2$phen]$^{n+}$ (II), provide a good basis for the comparison of the theory with experiment. We now report the measurement of the circular dichroism spectra of the complexes (I; M = N^{II})[9] (Figure 1), (I, M = OS^{II} or Os^{III})[10] (Figure 2) and (II; M = Os^{II} or Os^{III})[10] (Figure 3), and an analysis of the data based upon the exciton theory of optical activity (Table).

FIGURE 2 The absorption spectra (upper curves) and circular dichroism (lower curves) of (+)$_{546}$-[Os phen$_2$bipy]$^{2+}$ (———) and of (+)$_{546}$-[Os phen$_2$bipy]$^{3+}$ (— — —) in water
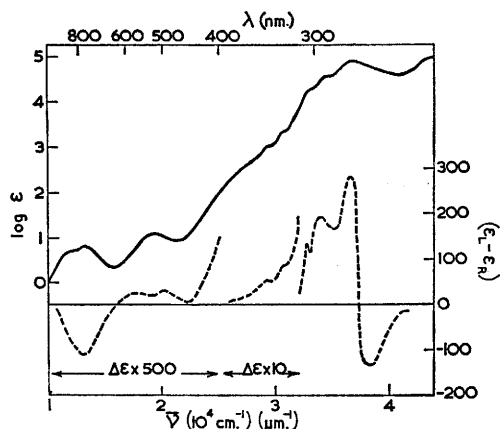

FIGURE 1 The absorption spectrum (———) and the circular dichroism (— — —) of (+)-[Ni phen$_2$bipy]$^{2+}$ in water

The Exciton States of Hetero-trischelated Complexes.— In a hetero-trischelated complex, [M(L$_a$L$_b$L$_c$)], where M is a transition-metal ion and L is a symmetrical bidentate ligand with L$_a$ = L$_b$ ≠ L$_c$, the only element of symmetry, apart from the identity, is the two-fold rotation axis of the ligand L$_c$ and the electronic states belong to either the A or the B representation. If each ligand has

[9] J. A. Broomhead and F. P. Dwyer, *Austral. J. Chem.*, 1962, **15**, 453.

[10] D. A. Buckingham, F. P. Dwyer, H. A. Goodwin, and A. M. Sargeson, *Austral. J. Chem.*, 1964, **17**, 325.
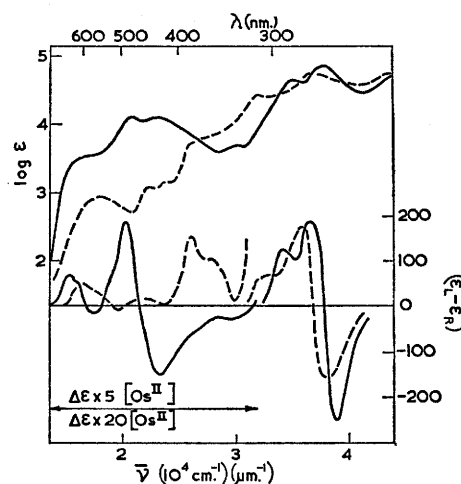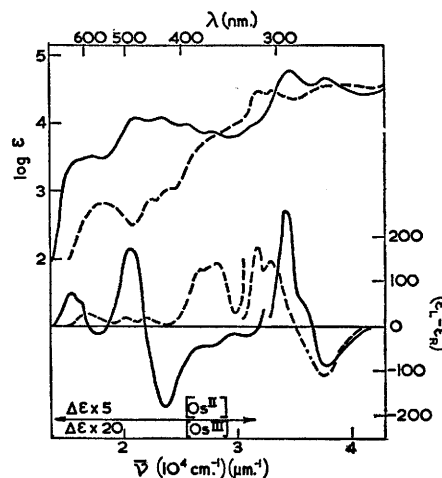

FIGURE 3 The absorption spectra (upper curves) and the circular dichroism (lower curves) of (+)$_{546}$-[Os bipy$_2$phen]$^{3+}$ (———) and of (+)$_{546}$-[Os bipy$_2$phen]$^{3+}$ (— — —) in water

by the linear combination of the locally excited configurations,

$$\psi_1(A) = (\phi_a'\phi_b - \phi_a\phi_b')\phi_c/\sqrt{2} \tag{2}$$

$$\psi_1(B) = \cos\alpha(\phi_a'\phi_b + \phi_a\phi_b')\phi_b/\sqrt{2} + \sin\alpha\phi_a\phi_b\phi_c' \tag{3}$$

and

$$\psi_2(B) = \sin\alpha(\phi_a'\phi_b + \phi_a\phi_b')\phi_c/\sqrt{2} - \cos\alpha\phi_a\phi_b\phi_c' \tag{4}$$

The functions $\psi_1(B)$ and $\psi_2(B)$ represent stationary states if,

$$\langle\psi_1(B)|\mathscr{H}|\psi_2(B)\rangle = 0 \tag{5}$$

where $\mathscr{H}$ is the complete Hamiltonian of the complex, given by equation (10) of the preceding paper, Part XII.[1] The stationary-state condition (equation 5) determines the mixing coefficients [11] of the B states, sin α, and cos α, through the relationship,

$$\tan 2\alpha = 2\sqrt{2}V_{ac}/(\bar{v}_a - \bar{v}_c + V_{ab}) \tag{6}$$

where V_{ab} and V_{ac} are the exciton splitting energies between similar and dissimilar ligands, respectively (equation 16 of Part XII), and $\bar{v}_a$ and $\bar{v}_c$ are the frequencies of the transitions $\phi_a \rightarrow \phi_a'$ and $\phi_c \rightarrow \phi_c'$, respectively, in the free ligand, both sets of quantities being expressed in wavenumbers.

The exciton splitting energies in the complexes (I) and (II) have been obtained from the electrostatic interaction between the transition monopole distributions (equation 21 of Part XII) of the excitations giving the long-axis polarised p-band of phenanthroline and bipyridyl. The p-band arises primarily from the excitation $\pi_6 \rightarrow \pi_7$ and $\pi_7 \rightarrow \pi_8$ in bipyridyl and phenanthroline, respectively, and the atomic orbital coefficients

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* In the empirically based exciton treatment adopted here the rotational strength of a transition to an exciton state $\psi(\Gamma)$, belonging to the representation Γ (equations 2—4) is a sum of triple scalar product terms which represent pair-wise interactions between the electric dipole exciton moments ρ of the individual ligands, L_a, L_b, L_c,

$$R(\Gamma) = \pi\sum_{a,b,c} C_a\Gamma C_b\Gamma[\vec{\rho_a} \cdot (\vec{r_{ab}} \times \vec{\rho_b})\bar{v}_b] \tag{9a}$$

the sum being taken over all ligand-pairs. The coefficients, $C_a\Gamma$ and $C_b\Gamma$, express the respective contributions of the excited configurations, $\phi_a'\phi_b\phi_c$ and $\phi_a\phi_b'\phi_c$, to the exciton state $(\psi(\Gamma)$ (equations 2—4), and the term in square brackets represents the scalar product of the point electric dipole excitation moment, $\vec{\rho_a}$, with the contribution to the magnetic-dipole transition moment, $\pi\bar{v}_b(\vec{r_{ab}}\vec{x}\vec{\rho_b})$, due to the electric moment $\vec{\rho_b}$. The vector $\vec{r_{ab}}$ defines the position of $\vec{\rho_b}$ relative to an origin at $\vec{\rho_a}$. In reducing the triple scalar products to algebraic products and summing the terms of equation (9a) to obtain expressions for the rotational strengths of hetero-trischelated complexes in the exciton approximation (equations 7—9) the distances, r_{ab}, r_{bc}, r_{ac}, have been expressed in terms of r_{ML}, the distance from the metal ion to the assumed location of the point excitation dipole ρ at the centre of the internuclear bond of bipyridyl or of the corresponding bond of phenanthroline, and the quantities $\bar{v}$ and ρ have been obtained empirically from the absorption spectrum of the free ligand.

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of these molecular π-orbitals, calculated in the Hückel approximation with a Coulomb integral increment for the nitrogen atoms of $\Delta\alpha_N = 0.5\beta$, give $V_{ab} = +700$ cm.$^{-1}$ for two phenanthroline ligands, $V_{ac} = +850$ cm.$^{-1}$ for a bipyridyl and a phenanthroline ligand, and $V_{ab} = +970$ cm.$^{-1}$ for two bipyridyl ligands. The structure of the complexes (I) and (II) adopted for these calculations was based upon that of [Fe phen$_3$]$^{2+}$ determined by X-ray diffraction.[2] The estimates of V_{ab} and V_{ac} based upon Hückel orbitals obtained with $\Delta\alpha_N = 0.5\beta$ are conservative, as a larger Coulomb integral is the more appropriate for nitrogen atoms bearing a partial positive charge, which results in a larger exciton splitting.[1] However, the effects of metal–ligand π-bonding, which diminishes the apparent exciton splitting,[1] are to some degree compensated empirically by the adoption of the lower set of values, for V_{ab} and V_{ac}. The configurational mixing coefficients of the B states (equations 3 and 4), obtained from these values (equation 6) are $\alpha = +19.85°$ for complex (I) and $\alpha = -31.65°$ for complex (II), compared with $\alpha = +35.27°$ for a homo-trischelated complex with D_3 symmetry.

The frequencies and dipole and rotational strengths of the transitions of the complexes (I) and (II) deriving from the coupling of the ligand p-band excitations are dependent upon the values of the configurational mixing coefficients. For the $P(C_2)$ configuration of the complexes (I) and (II), which is related to the $M(C_3) P(C_2)$ configuration established [2] for (−)-[Fe phen$_3$]$^{2+}$, the rotational strengths are given by the relations,

$$R(A) = +\pi r_{ML}\bar{v}_a D_a/\sqrt{2} \tag{7}$$

$$R_1(B) = -\pi r_{ML}[\sqrt{2}\bar{v}_a D_a \cos^2\alpha + (\bar{v}_a + \bar{v}_c)\sin 2\alpha\sqrt{(D_a D_c)}]/2 \tag{8}$$

and

$$R_2(B) = -\pi r_{ML}[\sqrt{2}\bar{v}_a D_a \sin^2\alpha - (\bar{v}_a + \bar{v}_c)\sin 2\alpha\sqrt{(D_a D_c)}]/2 \tag{9}$$

where D_a and D_c are the dipole strength of the p-band in the spectrum of the free ligand, L_a and L_c, respectively, and r_{ML} is the distance between the metal ion and the assumed location of the point-excitation dipole in each ligand of the complex, namely, the centre of the internuclear bond in bipyridyl or of the corresponding bond in phenanthroline. The dipole strengths of the p-band of bipyridyl and phenanthroline are 14 and 30, respectively, in units of 10^{-36} c.g.s. and r_{ML} is taken as 2.63 Å.*

The corresponding expressions for the dipole strengths of the resultant transitions of the complexes (I) and (II) are,

$$D(A) = D_a/2 \tag{10}$$

$$D_1(B) = (3/2)D_a \cos^2\alpha + D_c \sin^2\alpha + \cos\alpha \sin\alpha \sqrt{2D_a D_c} \tag{11}$$

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[11] T. Förster, 'Modern Quantum Chemistry,' Istanbul Lectures, pt. III, ed. O. Sinanoglu, Academic Press, New York, 1965, p. 93.

and

$$D_2(B) = (3/2)D_a \sin^2 \alpha + D_c \cos^2 \alpha -$$
$$\cos \alpha \sin \alpha \sqrt{2D_aD_c} \quad (12)$$

Thus the rotational and dipole strengths of (I) and (II) follow the sum rules,

$$R(A) + R_1(B) + R_2(B) = 0 \quad (13)$$

and

$$D(A) + D_1(B) + D_2(B) = 2D_a + D_c \quad (14)$$

Finally, the state wavefunctions (equations 1—4) and the augmented Hamiltonian (equation 10 of Part XII)
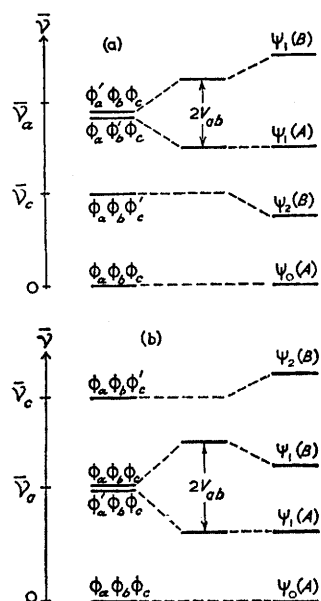

FIGURE 4 The exciton-splitting pattern of the long-axis polarised ligand excitations in a hetero-trischelated complex [M(L_aL_bL_c)], (a) for the case where the excitation energy of the dissimilar ligand L_c lies below that of the similar ligands, L_a and L_b, e.g. [M phen_2bipy]^{n+}, and (b) for the case where the excitation energy of the dissimilar ligand L_c lies above that of the similar ligands, L_a and L_b, e.g. [M bipy_2phen]^{n+}

of the trischelated complexes give the frequencies of the resultant transitions of (I) and (II) through the expressions,

$$\bar{\nu}(A) = \bar{\nu}_a + (U'_{ab} - U_{ab}) +$$
$$(U'_{ac} - U_{ac}) - V_{ba} \quad (15)$$

$$\bar{\nu}_1(B) = \bar{\nu}_a \cos^2 \alpha + \bar{\nu}_c \sin^2 \alpha + (U'_{ab} - U_{ab}) \cos^2 \alpha +$$
$$(U'_{ac} - U_{ac})(1 + \sin^2 \alpha) +$$
$$V_{ab} \cos^2 \alpha + \sqrt{2} \sin 2\alpha V_{ac} \quad (16)$$

and

$$\bar{\nu}_2(B) = \bar{\nu}_a \sin^2 \alpha + \bar{\nu}_c \cos^2 \alpha + (U'_{ab} - U_{ab}) \sin^2 \alpha +$$
$$(U'_{ac} - U_{ac})(1 + \cos^2 \alpha) +$$
$$V_{ab} \sin^2 \alpha - \sqrt{2} \sin 2\alpha V_{ac} \quad (17)$$

where the energies U and U' represent the Coulombic

interaction between the charge density distribution in two ligands of the complex, both in the electronic ground-state in the case of U (equation 14 of Part XII) and one in the ground-state and the other in the excited-state for U' (equation 15 of Part XII). In the homo-trischelated complexes the quantities $(U' - U)$ contribute only a common frequency-shift to the transitions arising from the set of three similar ligand excitations (equations 12 and 13 of Part XII), but in the hetero-trischelated complexes these quantities are different for the three resultant transitions and contribute in principle to the frequency intervals between them (equations 15—17). However, for ligands as similar as phenanthroline and bipyridyl the difference between the quantities $(U'_{ab} - U_{ab})$ and $(U'_{ac} - U_{ac})$, which are in themselves small, is probably negligible, and only the frequencies, $\bar{\nu}_a$ and $\bar{\nu}_c$, and the monopole exciton energies, V_{ab} and V_{ac}, have been considered in evaluating (equations 15—17) the theoretical frequencies of the complexes (I) and (II) recorded (Table, Figure 4).

DISCUSSION

The exciton theory of optical activity applied to the complexes [M phen_2bipy]^{n+} and [M bipy_2phen]^{n+} indicates that in the absorption region 30,000—40,000 cm.^{-1} of the long-axis polarised p-bands of bipyridyl and phenanthroline the isomers with the configurations (I) and (II) are expected to give rise to two positive and one negative circular dichroism band, the latter lying at the highest frequency (Table). The major of the two positive circular dichroism bands, with the rotational strength $R(A)$, is placed at the higher frequency in the case of complexes of the type (I) (Figure 4a) whereas this band lies at the lower frequency in complexes of the type (II) (Figure 4b). The experimental circular dichroism spectra of the isomers studied (Figures 1—3) in the 30,000—40,000 cm.^{-1} region are in accord with these requirements, and the relative values, although not the absolute magnitudes, of the rotational strengths and the frequencies of the circular dichroism bands are in fair agreement with the calculated values (Table).

The two positive circular dichroism bands given by the complexes (I) and (II) in the 30,000—40,000 cm.^{-1} region derive in large measure from the positive dichroism absorption in the same region of the corresponding homo-trischelated complex with the related $M(C_3) P(C_2)$ configuration,[1] due to the degenerate exciton transition, $\psi_0(A_1) \to \psi_{1,2}(E)$ (equations 1, 3, and 4 of Part XII). The exciton state of the hetero-trischelated complexes, $\psi_1(A)$ (equation 2), has the same form as the corresponding dihedral function, $\psi_1(E)$ (equation 3 of Part XII), and the exciton transition responsible for the major of the two positive circular dichroism bands of the complexes (I) and (II), $\psi_0(A) \to \psi_1(A)$, has a frequency and a dipole and rotational strength which are governed solely by the absorption properties of the two similar ligands, L_a and L_b, and are independent of those of the dissimilar ligand, L_c, and of the configurational mixing

coefficients which enter the expressions for the exciton states with B symmetry (equations 3 and 4). In consequence for related hetero- and homo-trischelated complexes, such as $[M\ phen_2\ bipy]^{n+}$ and $[M\ phen_3]^{n+}$ or $[M\ bipy_2phen]^{n+}$ and $[M\ bipy_3]^{n+}$, we have the relations,

$$\bar{\nu}(A) = \bar{\nu}(E) \qquad (18)$$

and

$$R(A) = \pm R(E)/2 \qquad (19)$$

the positive and the negative sign referring to isomers with the same and opposed configurations, respectively. The experimental data for the divalent complexes studied are in satisfactory agreement with the relations (18) and (19), although the rotational strengths of the trivalent complexes (I) and (II) are somewhat low (see Table, and Table 1 of Part XII).

As the frequency and dipole and rotational strength of the exciton transition $\psi_0(A) \to \psi_1(A)$ of a hetero-trischelated complex $[M(L_aL_bL_c)]$ are invariant for changes in the absorption properties of the dissimilar ligand, L_c, the absolute configuration of such complexes may be determined without recourse to detailed calculations. In all cases $R(A)$ is positive for the $P(C_2)$ configuration (I) and (II), and for a wide range of the configurational coupling coefficients, $\sin \alpha$ and $\cos \alpha$, connecting the B exciton states (equations 3 and 4), the major of the two dichroism bands with the same sign in the exciton triad arises from the $\psi_0(A) \to \psi_1(A)$ transition. If the dissimilar ligand L_c absorbs at a higher frequency than the similar ligands L_a and L_b, $\bar{\nu}(A)$ lies below $\bar{\nu}_1(B)$ and $\bar{\nu}_2(B)$ (Figure 4b), but if the absorption of L_c falls at a lower frequency than that of L_a and L_b, then $\bar{\nu}(A)$ lies between $\bar{\nu}_1(B)$ and $\bar{\nu}_2(B)$ (Figure 4a).

For the long-axis polarised excitations of the common bidentate π-electron ligands co-ordinated octahedrally in a hetero-trischelate complex the exciton splitting energies, V_{ab}, and V_{ac} are positive, and under the limiting condition, $V_{ac} \gg (\bar{\nu}_a - \bar{\nu}_c + V_{ab})$, particularly in conjunction with the inequality, $D_c > D_a$, we have for the $P(C_2)$ configuration of the complexes (I) and (II) $R_2(B) > R(A)$ or $R_1(B) > R(A)$, depending upon the positive or the negative sign, respectively, of $(\bar{\nu}_a - \bar{\nu}_c + V_{ab})$ (equations 6—9). In this eventuality the major of the two circular dichroism bands with a common sign, positive for the $P(C_2)$ configuration, lies at the lowest frequency and the minor of the two bands, due to the $\psi_0(A) \to \psi_1(A)$ exciton transition is placed at he intermediate frequency (equations 15—17). The properties of the complexes (I) and (II) lie outside this limiting condition, which may be realised, however, in complexes $[M(L_aL_bL_c)]$ where L_a and L_b are phenanthroline and L_c an appropriately substituted phenanthroline ligand, or in analogous hetero-trischelated complexes.

In the converse limiting case where $V_{ac} \ll (\bar{\nu}_a - \bar{\nu}_c + V_{ab})$ the circular dichroism spectrum of the hetero-trischelated complex resembles that of the corresponding homo-bischelated complex. The exciton interaction of the similar ligands L_a and L_b with the dissimilar ligand L_c becomes negligible compared with that between the similar ligands, and for the mixing coefficients of the exciton states with B symmetry (equations 3 and 4) we have $\cos \alpha \to 1$ and $\sin \alpha \to 0$, or the converse, depending upon the choice of phase. The bisphenanthrolineoxalato- and bisbipyridyloxalato-complexes of chromium(III),[12] for example, give two dichroism bands of opposite sign and nearly equal area in the region of the heterocyclic ligand p-band absorption,[13] as anticipated for a homo-bischelated complex.[14] There are no evident indications of exciton interaction between the oxalato- and the heterocyclic ligands in these complexes, owing to the large value (ca. 15,000 cm.$^{-1}$) of the frequency interval $(\bar{\nu}_a - \bar{\nu}_c)$, in contrast to the case of the complexes (I) and (II) where the frequency separation between the p-band excitations of the different ligands is only 2200 cm.$^{-1}$.

The requirements of the exciton theory in regard to the dipole strengths of the transitions of the complexes (I) and (II) arising from the ligand p-band excitations show less satisfactory agreement with experiment than the expectations referring to the frequencies and rotational strengths (Table). In general exciton interaction between the long-axis polarised ligand excitations of a hetero-trischelated complex transfers dipole strength from the absorption region of the ligand or ligands with the lower excitation energy to that of the ligand or ligands with the higher transition frequency (Table), owing to the particular mutual stereochemical disposition of the ligands in the complex produced by octahedral six-co-ordination. Experimentally the anticipated degree of transfer of dipole strength is not observed, nor is the sum rule for dipole strengths (equation 14) obeyed, whereas the sum rule for rotational strengths (equation 13) is followed in fair approximation (Table). The sum of the dipole strengths for the ligand p-band excitations in the complexes (I) and (II) is significantly larger than the corresponding sum for the free ligands in the case of the osmium(II) complexes which exhibit intense metal–ligand charge-transfer bands in the visible region (Figure 2 and 3). Bipyridyl and phenanthroline possess a series of unoccupied π-orbitals of increasing energy and it is probable that one or more of the higher-energy metal–ligand charge-transfer transitions lie in the same frequency range as the ligand p-band absorption. The charge-transfer transitions are polarised predominantly in the direction of the shorter in-plane axis of the ligand,[1,15-17] and whilst they augment the dipole strength observed in the p-band region they do not contribute significantly to the rotational strength.

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In addition the α- and the p-band excitations of phenanthroline overlap, and the former contributes a minor short-axis polarised component to the absorption observed in the p-band region.[1] Exciton interaction between short-axis polarised ligand excitations in a hetero-trischelated complex transfers dipole strength from the absorption region of the ligand with the higher transition frequency to that of the ligand with the lower excitation energy, contrary to the effect of the coupling of long-axis polarised ligand transitions in an octahedrally co-ordinated trischelate complex. Thus we find that the observed dipole strengths of the lower and the higher frequency exciton transitions of the hetero-trischelated complexes (I) and (II) are too large and too small, respectively, in relation to the theoretical values (Table 1), which were calculated on the assumption that the exciton transitions in the ligand p-band region result wholly from long-axis polarised ligand excitations. From the discrepancies it is concluded that short-axis polarised excitations of a charge-transfer and internal ligand origin augment the isotropic absorption of the complexes (I) and (II) in the 30,000—40,000 cm.$^{-1}$ region, although the primary contribution arises from long-axis polarised ligand

excitations which are the principal determinant of the frequencies and the rotational strengths of the circular dichroism bands observed in this region.

EXPERIMENTAL

Spectra.—Measurements were made on aqueous solutions of the perchlorates of the complex ions maintained at 4° in the case of the nickel(II) complex. Circular dichroism spectra were measured with a Jouan Dichrograph and with an automatic recording version of a laboratory-constructed instrument described previously.[18] Isotropic absorption spectra were obtained with a Unicam SP 700 spectrophotometer. Rotational and dipole strengths (Table) were estimated by standard methods.[19]

[18] S. F. Mason, *Mol. Phys.*, 1962, **5**, 343.
[19] S. F. Mason, *Quart. Rev.*, 1963, **17**, 20.