Optical Rotatory Power of Co-ordination Compounds. Part XVI.† Intermediate Exciton Coupling in the Circular Dichroism of Trisbipyridyl Complexes

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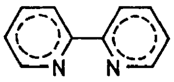
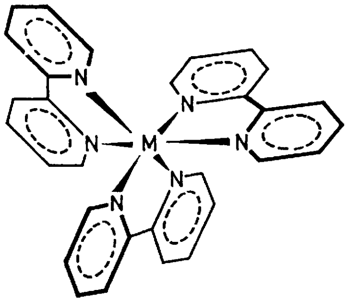
The circular dichroism of the trisbipyridyl complex of nickel(II) and of other transition-metal ions in the frequency region of the ligand π-electron absorption has been re-examined using an intermediate exciton coupling treatment in order to account for the observed vibronic structure. Contrary to an earlier report, it is found that the exciton splitting energy required to account for the observed magnitude of the circular dichroism and for the vibronic structure has a value comparable to that used in the strong-coupling treatment. For both the intermediate and the strong coupling method, the exciton energy is positive, giving positive and negative exciton c.d. bands at lower and higher frequency, respectively, in the case of complexes with the Λ-configuration. The analogous exciton c.d. absorption of the trisphenanthroline–metal complexes is found to approximate generally to the strong-coupling case.

In previous papers of this series [1,2] (Parts XII and XIII) exciton theory was applied to the π-electron excitations of the ligands in chiral trisbipyridyl and trisphenanthroline complexes of the iron-group metal ions in order to derive the absolute stereochemical configuration of a given complex from its electronic absorption and circular dichroism spectrum. The diagnostic excitations are those which are long-axis polarised in an individual ligand molecule, *i.e.* directed along the 4,4′-axis of 2,2′-bipyridyl (I) or the 3,8-direction in 1,10-phenanthroline, so that the excitation moment lies parallel to the octahedral edge spanned by the chelate ring in a complex. These are the lowest-energy excitations with a large absorption intensity, and they lie [1,2] at 35 and 37 kK in the case of 2,2′-bipyridyl and 1,10-phenanthroline, respectively.



(I)



(II)

The three long-axis moments in a tris-chelated complex couple Coulombically to give a resultant non-degenerate transition with A_2 symmetry and a doubly-degenerate transition with E symmetry in the D_3 group of the complex. The two resultant transitions have zero-order rotational strengths, R, which are given for the Λ-configuration (II) in the point-dipole approximation by,

$$R(E) = -R(A_2) = \sqrt{2}\pi\bar{\nu}_0 r_{\mathrm{LM}} D_0 \qquad (1)$$

where $\bar{\nu}_0$ and D_0 are, respectively, the wavenumber and the dipole strength of a long-axis polarised excitation in the free ligand or a mono-chelate complex and r_{ML} is the distance in the complex from the metal ion to the point excitation dipole, *e.g.* the centre of the internuclear bond in bipyridyl (I). In the same approximation, where only the coupling of isoenergetic ligand excitations is considered, the dipole strengths of the resultant transitions in a tris-chelated complex are:

$$D(A_2) = 2D(E) = 2D_0 \qquad (2)$$

The assignment of absolute configuration to a tris-chelated complex depends upon the frequency-order of the two oppositely-signed c.d. bands corresponding to $R(E)$ and $R(A_2)$ [equation (1)]. For octahedral co-ordination the Coulombic potential between the three long-axis ligand excitations gives the non-degenerate coupling mode the higher energy in the absence of π-electron exchange between the ligands, and

$$[\bar{\nu}(A_2) - \bar{\nu}(E)] = 3V \qquad (3)$$

where V is the exciton splitting energy, a quantity expressed here in wavenumbers. The exciton energy, V, is evaluated either theoretically by MO methods or empirically in the point dipole approximation through,

$$hcV = D_0/4(r_{\mathrm{ab}})^3 \qquad (4)$$

where r_{ab} is the distance between the point excitation dipoles of ligand $\mathrm{L_a}$ and ligand $\mathrm{L_b}$, *e.g.* the distance between the centres of the internuclear 2–2′ bonds of two of the ligands in a trisbipyridyl complex.

The sign of the frequency-interval [equation (3)] is crucial for the assignment of configuration, and the interval is positive with certainty only on the assumption, adopted in earlier work,[3-5] that there is no π-electron delocalisation between the ligands in a tris-chelated complex. The assumption was relaxed in Parts XII

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† Part XV, S. F. Mason, *J. Chem. Soc.* (*A*), 1971, 667.

[1] A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.* (*A*), 1969, 1428.

[2] S. F. Mason and B. J. Norman, *J. Chem. Soc.* (*A*), 1969, 1442.

[3] A. J. McCaffery and S. F. Mason, *Proc. Chem. Soc.*, 1963, 211.

[4] E. Larsen, S. F. Mason, and G. H. Searle, *Acta Chem. Scand.*, 1966, **20**, 191.

[5] J. Mason and S. F. Mason, *Tetrahedron*, 1967, **23**, 1919.

and XIII and the perturbations arising from π-delocalisation due to the overlap both of the π-orbitals of different ligands and of each ligand π-orbital with the $d\pi$-orbitals of the metal in a complex ion were estimated to first order. It was found [1,2] that these two perturbations do not affect the qualitative conclusions of the simple exciton treatment of bipyridyl and phenanthroline complexes. The results of π-SCF calculations on the trisphenanthroline [6-8] and trisbipyridyl [9,10] complexes of iron(II) similarly support the qualitative conclusions of the simple treatment and show that a third factor, the neglect of Coulombic interactions between ligand excitations of different energy in that treatment, is not important for stereochemical applications.

However, attention has been drawn [11,12] to a fourth factor, the effective reduction of the exciton splitting energy by vibronic interactions, which is judged [13] to have a significance that nullifies the generality of the conclusions in Parts XII and XIII. Vibronic effects are important in the weak and intermediate coupling cases of exciton theory.[14-17] These cases are distinguished from the purely electronic or strong coupling case, where such a distinction is possible, by the relative magnitudes of the electronic exciton energy, V, and the frequency of an upper-state vibrational mode, ω, appearing as a progression in the electronic spectrum of the monomeric ligand molecule. Förster has argued [15] that if the monomer absorption band has little or no vibrational structure, due either to the dominance of the 0–0 vibronic transition or to the broadness of each vibronic band in the progression, such that the sum of the vibronic band widths equals or exceeds the electronic band width, the distinctions between the sub-cases vanish and all three reduce to the strong-coupling case. Since the absorption bands of phenanthroline and bipyridyl and their mono-chelate complexes in solution at room temperature show only weakly developed vibronic structure (Figure 1), the strong-coupling exciton formalism was employed in Parts XII and XIII and vibronic effects were neglected.

If the electronic absorption band of the monomer has a well-developed vibronic structure the strong, weak, and intermediate coupling cases become distinct for the corresponding dimer or trimer. The strong coupling case obtains when $V > \omega$ and the weak when $\omega \gg V$. In the weak coupling case the effective exciton splitting energy is reduced, being $V(S_{0n})^2$ for the n-th member of the progression, where S_{0n} is the Franck–Condon overlap between the zero vibrational level of the electronic ground state and the n-th vibrational level of the electronic excited state.[14-17] The electronic excitation energy due to the absorption of a photon is transferred from one ligand to another within a vibrational period in the strong coupling case, so that none of the ligands in a complex relax to the equilibrium nuclear configuration of the excited state of the free ligand, whereas in the weak coupling case each ligand of the complex relaxes to that equilibrium nuclear configuration before the excitation energy is transferred, resulting in a reduced effective exciton splitting and a double minimum in the potential-energy curve of one of the two coupled exciton states.[15-17]

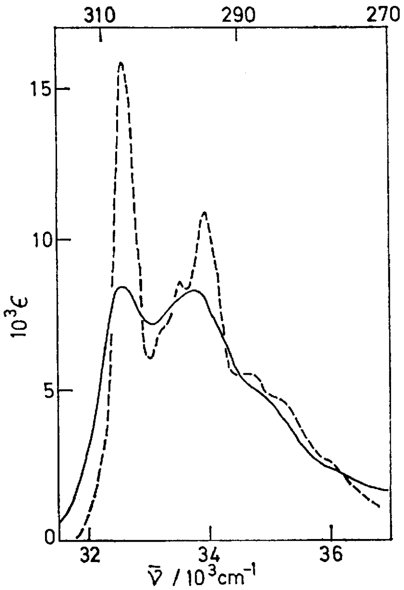

FIGURE 1 The absorption spectrum of $[Zn(bipy)]^{2+}$ in EtOH–MeOH, 4 : 1, at ambient (——) and liquid-nitrogen temperature (– – – –).

For the intermediate coupling case, where $\omega > V$, the effective exciton splitting is similarly reduced. The lower-energy excited electronic state of an exciton-coupled dimer [16] or trimer [17] has a regular vibronic structure, but that of the higher-energy state is irregular, being a complex function of the exciton energy, V, the force constant and the frequency, ω, of the vibrational mode of the monomeric ligand, and the displacement of the equilibrium nuclear co-ordinates of the ligand due to the electronic excitation. Computer programmes for calculating the theoretical vibronic spectrum of an exciton-coupled dimer [16] or trigonal trimer [17] in the intermediate coupling case have been developed by

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[6] I. Hanazaki and S. Nagakura, *Bull. Chem. Soc. Japan*, 1969, **42**, 702; *Inorg. Chem.*, 1969, **8**, 654.

[7] N. Sanders and P. Day, *J. Chem. Soc.* (*A*), 1970, 1190.

[8] N. Sanders, *J. Chem. Soc.* (*A*), 1971, 1563; *J.C.S. Dalton*, 1972, 345.

[9] I. Hanazaki and S. Nagakura, *Inorg. Chem.*, 1969, **8**, 648 and 654.

[10] N. Sanders, unpublished work.

[11] R. G. Bray, J. Ferguson, and C. J. Hawkins, *Austral. J. Chem.*, 1969, **22**, 2091.

[12] C. J. Hawkins, 'Absolute Configuration of Metal Complexes,' Wiley-Interscience, London, 1971, ch. 5.

[13] Ref. 12, p. 242.

[14] A. S. Davydov, 'Theory of Molecular Excitons,' trans. M. Kasha and M. Oppenheimer, McGraw-Hill, London, 1962.

[15] Th. Förster, 'Modern Quantum Chemistry, Part III,' ed. O. Sinanoglu, Academic Press, London, 1965, p. 93.

[16] R. L. Fulton and M. Gouterman, *J. Chem. Phys.*, 1961, **35**, 1095; 1964, **41**, 2280.

[17] M. H. Perrin and M. Gouterman, *J. Chem. Phys.*, 1967, **46**, 1019.

Gouterman and his co-workers. The programmes employ the dimensionless quantities,

$$\varepsilon = (V/\omega);\ \lambda^2 = (\Delta E/\omega);\ \text{and}\ \alpha = (\Delta\omega/\omega) \qquad (5)$$

both energy and frequency being expressed here in wavenumbers. ΔE Is the energy required to adjust the monomeric ligand from its equilibrium nuclear configuration in the electronic ground state to that of the corresponding excited state. The parameter, λ^2, is given empirically by the intensity ratio of the 0–1 to the 0–0 member of the vibronic progression in the electronic absorption spectrum of the monomer ligand, and $\Delta\omega$ is the Gaussian half-width of each vibronic band in the progression.

The trimer programme [17] has been used by Hawkins and his co-workers [11,12] to calculate the theoretical absorption spectrum of a tris-chelated complex for the parameter values, $\lambda = 0{\cdot}9$ and $\alpha = 0{\cdot}2$ with ε ranging from $\pm 0{\cdot}1$ to $\pm 1{\cdot}0$, and the theoretical circular dichroism of a complex with the Δ-configuration for $\lambda = 0{\cdot}9$, $\alpha = 0{\cdot}5$, and $\varepsilon = +0{\cdot}05$. The calculated c.d. is judged to be in good accord with the experimental c.d. of (−)-$[\mathrm{Ni(bipy)_3}]^{2+}$ in alcohol solution at room temperature over the 30—38 kK region, confirming the assignment [18] of the Δ-configuration to this complex. Hawkins and his co-workers conclude that, with $\omega = 1400\ \mathrm{cm^{-1}}$, the exciton splitting energy is much smaller ($V = +70\ \mathrm{cm^{-1}}$) than calculated empirically in the point dipole approximation [equation (4)] or theoretically by MO methods and that, in the general case, even the sign of V cannot be reliably determined by those procedures.

However, the comparison made by Hawkins and his co-workers between the calculated and theoretical c.d. curves is purely qualitative, and reference to their illustrations of theoretical rotational strength as a function of frequency [19] shows that $R(A_2)$ and $R(E)$ overlap over more than 90% of the total band area for the parameter values chosen. Since $R(A_2)$ and $R(E)$ have opposite signs they mutually cancel in the region of overlap and the experimental c.d. band areas are then expected to give empirical rotational strengths no larger than 10% of the theoretical values obtained from equation (1) using the experimental dipole strength of the monomer ligand absorption. In fact the major exciton c.d. bands of trisbipyridyl and trisphenanthroline complexes near 33 and 37 kK, respectively, are found [1,18] to have rotational strengths averaging some 40% of the theoretical magnitude given by equation (1) from the experimental values of the frequency and the dipole strength of the corresponding absorption band of the free ligand.

The dissymmetry factor, expressing the ratio of the circular dichroism to the corresponding isotropic absorption,[20] shows more directly that the exciton rotational strengths, $R(A_2)$ and $R(E)$, of the trisbipyridyl and trisphenanthroline complexes overlap on the frequency scale and mutually cancel only to a limited degree. As the isotropic absorption of the complexes is unresolved the dipole strengths of the two exciton components, $D(A_2)$ and $D(E)$ [equation (2)], are individually inaccessible, but the sum may be measured directly from the corresponding total absorption band area.[21] The empirical rotational strengths, $R(A_2)$ and $R(E)$, are similarly obtained from the corresponding c.d. band area.[21] A dissymmetry factor, g, adapted from the normal expression,[20,21] is defined for the present purpose as,

$$g(E) = -g(A_2) = 4R(E)/[D(E) + D(A_2)] \qquad (6)$$

From the equations (1) and (2) the theoretical dissymmetry factor is given by,

$$g(E) = (4/3)\sqrt{2}\pi\bar{\nu}_0 r_{\mathrm{ML}} \qquad (7)$$

where $\bar{\nu}_0$ is the transition wavenumber for the monomer ligand, 35·6 and 37·5 kK for bipyridyl and phenanthroline, respectively, and r_{ML} is the distance between the metal ion and the centre of the internuclear 2,2′-bond of bipyridyl or the corresponding bond of phenanthroline. The value, $r_{\mathrm{ML}} = 2{\cdot}78$ Å, obtained from the bond lengths and bond angles reported [22,23] from X-ray crystal structure analyses of $[\mathrm{Ni(phen)_3}]^{2+}$ salts, gives the theoretical g-factor [equation (7)] a value of $6{\cdot}0 \times 10^{-3}$ for the trisphenanthroline complexes and $5{\cdot}8 \times 10^{-3}$ for the trisbipyridyl complexes. These g-factors would be reduced by an order of magnitude if the rotational strengths, $R(E)$ and $R(A_2)$, mutually cancelled to within 10%. However, Table 1 of Part XII shows [1] that the experimentally observed g-factors [equation (6)] average to $2{\cdot}2 \times 10^{-3}$ for the trisphenanthroline complexes and to $2{\cdot}8 \times 10^{-3}$ for the trisbipyridyl complexes, representing 36 and 48%, respectively, of the theoretical g-factor [equation (7)]. The MO studies [6-10] of the bipyridyl and phenanthroline complexes of iron(II) give theoretical g-factors which, by comparison with the corresponding experimental values,[1] show similarly that some 40% of the theoretical exciton rotational strengths appear in the observed c.d. spectra.

As the previous calculations [11] are quantitatively unsatisfactory we have employed the trimer programme [17] to determine the parameter values consistent with the appearance of some 40% of the theoretical exciton rotational strength [equation (1)] in the experimental c.d. spectrum of a trisbipyridyl complex in the 30—38 kK region. We find that the fraction of the theoretical rotational strength expected to appear in the c.d. spectrum is approximately proportional to the value of the adjustable parameter, ε, over the intermediate coupling range for given values of α and λ, which are determined from the vibronic bandwidth and the ratio of the 0–1 to the 0–0 vibronic intensities, respectively, in the ambient-temperature spectrum of the monobipyridylzinc(II) complex (Figure 1). The theoretical spectra illustrated (Figure 2) refer to the parameter values, $\lambda = 1{\cdot}0$, $\alpha = 0{\cdot}5$, and $\varepsilon = +0{\cdot}5$, and to the Λ-configuration (II) of the complex. The band areas of the

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[18] S. F. Mason, *Inorg. Chim. Acta Rev.*, 1968, **2**, 89.

[19] Ref. 11, p. 2100; ref. 12, p. 246.

[20] W. Kuhn, *Trans. Faraday Soc.*, 1930, **46**, 293.

[21] S. F. Mason, *Quart. Rev. Chem. Soc.*, 1963, **17**, 20.

[22] K. R. Butler and M. R. Snow, *J. Chem. Soc.* (*A*), 1971, 565.

[23] B. A. Frenz and J. A. Ibers, *Inorg. Chem.*, 1972, **11**, 1109.

individual rotational strengths, $R(A_2)$ and $R(E)$, are normalised to the theoretical values given by equation (1), and the total dipole strength band area is normalised analogously to the sum $[D(A_2) + D(E)]$, obtained from equation (2), and the dipole strength of the 35 kK bipyridyl absorption. The rotational strengths, $R(A_2)$ and $R(E)$, overlap and mutually cancel over nearly 60% of their band areas, so that some 40% of those strengths are expected to be observable for the parameter values taken. Comparison of the theoretical c.d. curve, given by the sum $[R(A_2) + R(E)]$, with the experimental c.d. of (+)-$[Ni(bipy)_3]^{2+}$ (Figure 2) indicates that the critical parameter, ε, has about the right value (+0·5) and that the previously advocated [11] value (+0·05) is too small.

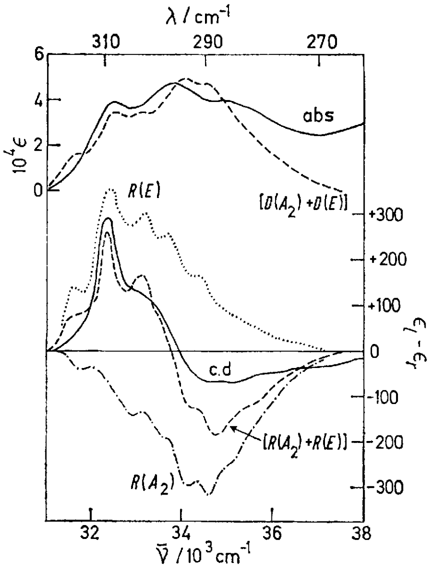

FIGURE 2 The absorption (upper curves) and circular dichroism (lower curves) obtained experimentally for (+)-$[Ni(bipy)_3]^{2+}$ in ethanol (——) and theoretically for the Λ-configuration of a trisbipyridyl complex (– – – –) for the intermediate-coupling parameter values, $\lambda = 1$, $\varepsilon = 0{\cdot}5$, and $\alpha = 0{\cdot}5$. The rotational strengths of the doubly-degenerate coupling mode, $R(E)$ (· · · ·), and the non-degenerate mode, $R(A_2)$ (— · — · —) are represented individually for these parameter values

The upper-state vibrational mode of bipyridyl considered in our calculation has a frequency of 700 cm^{-1}, which is taken from the low-temperature spectrum of the monobipyridyl–zinc(II) complex (Figure 1), so that the exciton splitting energy is +350 cm^{-1}. The frequency-interval between the A_2 and the E coupling mode of the long-axis polarised ligand excitations near 33 kK in a trisbipyridyl complex [equation (3)] accordingly has the value of +1050 cm^{-1}, in good agreement with the value of +1100 cm^{-1} obtained [10] from a π-SCF study of $[Fe(bipy)_3]^{2+}$, where it is concluded that the c.d. of this complex in the ligand π→π* frequency region is produced essentially by the exciton mechanism.

Vibronic interactions are neglected in the MO investigations [6-10] of the bipyridyl and phenanthroline complexes of iron(II), and these studies refer essentially to the strong coupling exciton case. However, the MO studies [6-10] are not limited by the neglect since the exciton c.d. bands of the trisbipyridyl complexes of the divalent iron-group metals are devoid of vibronic structure, even at 80 K, and so approximate to the strong coupling case. Moreover the value of the vibronic bandwidth parameter adopted in the previous [11] and the present intermediate coupling calculations, $\alpha = 0{\cdot}5$, which is dictated by the broadness of the vibronic bands of the monobipyridyl zinc(II) complex at ambient temperature (Figure 1), implies that we are working at the limit where the sum of the individual vibronic bandwidths equals the electronic bandwidth and all three exciton subcases are reducible to the strong-coupling case.[15] A still larger value of the bandwidth parameter, going beyond this limit, may be appropriate in the present case since the theoretical absorption and c.d. spectra for $\alpha = 0{\cdot}5$ show a more-developed vibronic structure than the corresponding experimental spectra of (+)-$[Ni(bipy)_3]^{2+}$ (Figure 2).

The more detailed vibronic structure of the theoretical spectra may arise, additionally or alternatively, from a limitation of the trimer programme [17] which considers only one active upper-state vibrational mode in any give calculation. Three such modes with frequencies of 700, 950, and 1400 cm^{-1} are observed in the low-temperature spectrum of the monobipyridyl–zinc(II) complex (Figure 1) and it is probable that other modes are active but remain as yet unresolved. In principle a full representation of the theoretical absorption and c.d. spectrum of a trisbipyridyl complex requires the weighted superposition of spectra calculated for each vibrational mode. The most important of the modes is identified by the expectation [17] that the vibronic structure of the lower-energy exciton transition of a trimer under intermediate coupling consists of a regular progression in the active vibration frequency whereas the higher-energy exciton transition has a complex and irregular vibronic structure, as is exemplified by $R(E)$ and $R(A_2)$, respectively (Figure 2). At low temperature the circular dichroism of (−)-$[Ni(bipy)_3]^{2+}$ due to the lower frequency exciton transition consists of two vibronic members separated by 700 cm^{-1} (Figure 3) and approximately the same vibronic interval is observed in the lower-energy exciton c.d. of a number of trivalent metal trisbipyridyl complexes even at ambient temperature (Figure 4). Thus the important upper-state vibrational mode active in the intermediate coupling of the ligand excitations has the 700 cm^{-1} frequency and is not the 1400 cm^{-1} mode employed by Hawkins and his co-workers.[11,12]

Like the trisbipyridyl complexes of the divalent iron-group metals, the trisphenanthroline transition-metal complexes give smooth exciton c.d. bands devoid of vibronic structure, even at low temperature, with the possible exception of the chromium(III) complex, which exhibits a structure with an interval of 1200 cm^{-1} in the lower-energy exciton c.d. band (Figure 5). The structure here may be vibronic or may arise from a metal–ligand charge-transfer transition close in energy to long-axis polarised π→π* excitation of phenanthroline at

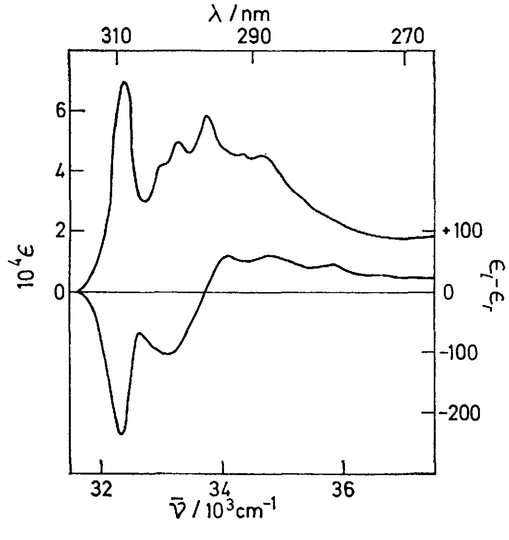

Figure 3 The absorption (upper curve) and c.d. spectrum (lower curve) of (−)-[Ni(bipy)$_3$]$^{2+}$ in EtOH–MeOH, 4 : 1, at liquid-nitrogen temperature

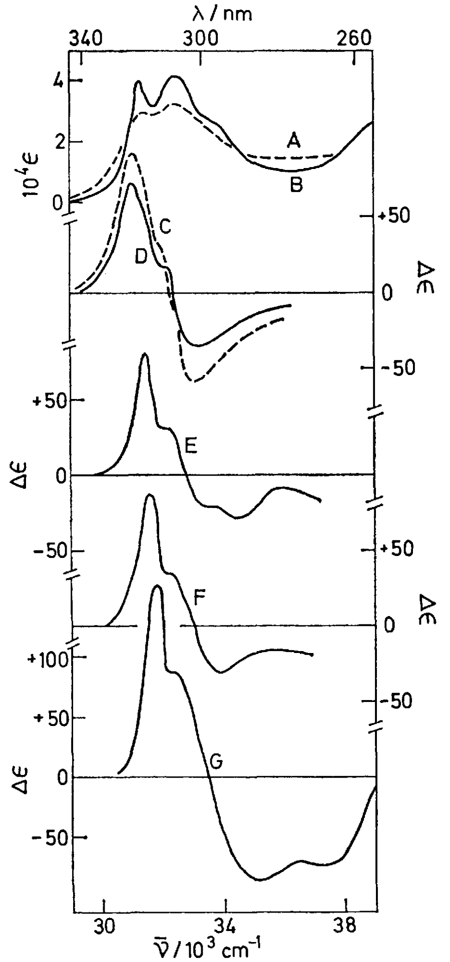

Figure 4 The absorption spectrum of [Co(bipy)$_3$]$^{3+}$ in EtOH–MeOH, 4 : 1, at (A) ambient and (B) liquid nitrogen temperature and the c.d. spectrum of (+)-[Co(bipy)$_3$]$^{3+}$ at (C) ambient and (D) liquid-nitrogen temperature, and the c.d. spectrum in water of (E) (+)-[Rh(bipy)$_3$]$^{3+}$ (F) (−)-[Ru(bipy)$_3$]$^{3+}$ and (G) (+)$_{546}$-[Os(bipy)$_3$]$^{3+}$.

37 kK, giving a superposed absorption and circular dichroism since the lower-energy of the two major c.d. bands is particularly broad in the case of (+)-[Cr(phen)$_3$]$^{3+}$ (Figure 5). In general the lower-energy of the two major exciton c.d. bands due to the E-coupling mode, has a smaller bandwidth than the corresponding higher energy c.d. band, due to the A_2-coupling mode, in both the trisbipyridyl and the trisphenanthroline metal complex series (Figures 3—5) due to the broad and irregular vibronic structure of the latter exciton transition under intermediate coupling (Figure 2). Thus the effect of vibronic interactions remains apparent in the narrowness of the lower-energy and the broadness of the higher-energy c.d. band of an exciton pair beyond the limit where the sum of the vibronic bandwidths equals the electronic bandwidth[15] and both c.d. bands are smooth and featureless.

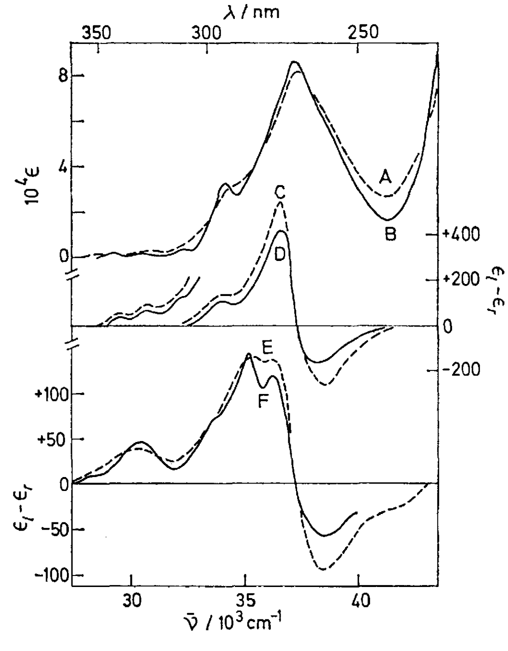

Figure 5 The absorption spectrum of [Ni(phen)$_3$]$^{2+}$ in EtOH–MeOH, 4 : 1, at (A) ambient and (B) liquid-nitrogen temperature and the c.d. spectrum of (+)-[Ni(phen)$_3$]$^{2+}$ at (C) ambient and (D) liquid-nitrogen temperature, and the c.d. spectrum of (+)-[Cr(phen)$_3$]$^{3+}$ in EtOH–MeOH, 4 : 1, at (E) ambient and (F) liquid-nitrogen temperature

The vibronic bandwidth parameter, α, and the exciton energy parameter, ε [equation (5)], are independent, and smooth exciton c.d. bands, indicating strong-coupling, do not necessarily imply that the exciton splitting energy, V, is large, nor that V has an appreciably different value in an analogous complex with exciton c.d. bands exhibiting vibronic structure. Thus the value of the frequency-interval between the A_2 and the E exciton coupling mode [equation (3)] of +1050 cm^{-1} obtained in the present work for [Ni(bipy)$_3$]$^{2+}$, which shows intermediate coupling, and of +1100 cm^{-1} calculated[10] for [Fe(bipy)$_3$]$^{2+}$, which exhibits strong-coupling, are probably representative of that interval in trisbipyridyl complexes generally. A frequency-separation [equation (3)] for trisphenanthroline complexes of the same sign and magnitude is consistent with the observation[1,18] that the exciton c.d. bands have rotational strengths with some 36% of the theoretical value calculated in the point-dipole approximation [equation (1)]. These c.d. bands have 33% of the total rotational strength calculated[8] by the π-SCF procedure, which gives a frequency-interval between the A_2 and E exciton states of +1200 cm^{-1}. A positive frequency-interval appears probable for all trisbipyridyl and trisphenanthroline metal complexes and, to the same degree of probability, the complexes exhibiting a positive lower-energy and a negative higher-energy exciton c.d. band, with or without vibronic structure, have the Λ-configuration (II).

EXPERIMENTAL

Materials.—These were prepared as described in the following paper (Part XVII).

Spectra.—Absorption spectra were obtained with a Unicam SP 700 and a Cary 14 spectrophotometer. Circular dichroism spectra were measured with a Jouan Dichrograph CD 185. Spectra at liquid-nitrogen temperature were obtained with solutions of the complex in an ethanol–methanol (4 : 1) glass. The reduced c.d. absorption at low-temperature may arise from some depolarisation of the radiation by strains in the glass.

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