Optical Rotatory Power of Co-ordination Compounds. Part XVII.† The Circular Dichroism of Trisbipyridyl and Trisphenanthroline Complexes

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The circular dichroism spectra of (+)-$[Cr(bipy)_3]^{3+}$, (+)-$[Rh(phen)_3]^{3+}$, (+)-$[Rh(bipy)_3]^{3+}$, (+)-$[Co(phen)_2(NO_2)_2]^+$, and (−)-$[Co(bipy)_2(NO_2)_2]^+$, are reported, and the corresponding spectra of trisbipyridyl and trisphenanthroline complexes previously studied have been remeasured over a more extended frequency range under higher resolution. The criteria proposed for determining the frequency-order of the principal exciton c.d. bands derived from the coupling of long-axis polarised ligand π-excitations are reappraised, and it is concluded that the methods based primarily on isotropic absorption data are contraindicated. A method based largely on the c.d. data is used to obtain the frequency-order, and thence the stereochemical configuration of a range of isomers in the bis- and tris-bipyridyl and -phenanthroline series.

In Parts XII [1] and XIII [2] of this series the absolute configuration of optical isomers in the trisbipyridyl and trisphenanthroline series of complexes of the iron-group metal ions was derived from an exciton analysis of their absorption and c.d. spectra. The analysis requires a knowledge of the energy-order of the degenerate and non-degenerate electronic transitions, with the respective symmetries of E and A_2 in the D_3 group of the tris-chelate complex, resulting from the coupling of the long-axis polarised π-excitations of the ligands. If π-electron exchange between the ligands is neglected, electrostatic interactions give the non-degenerate coupling-mode the higher energy, and,

$$[\bar{\nu}(A_2) - \bar{\nu}(E)] = 3V \qquad (1)$$

where V is the Coulombic potential between the π-excitation moments of two of the ligands in the complex. For octahedral co-ordination and for isoenergetic long-axis polarised ligand excitations, V is positive in the point dipole approximation, or in the Hückel MO approximation with π-delocalisation between the ligands and between a ligand and the metal ion taken into account to the first-order of perturbation theory.[1,2]

The results of π-SCF calculations on the trisphenanthroline [3-5] and trisbipyridyl [6,7] complexes of iron(II) show that V is indeed positive for the long-axis polarised ligand excitations in these complexes, but the generality of the conclusion has been questioned [8-10] and an alternative criterion for ordering the relative energies of the A_2 and E coupled exciton states of tris-chelate complexes containing conjugated ligands is proposed.[9,10] From an intermediate-coupling exciton treatment of vibronic interactions, reassessed in the preceding paper,[11] it is suggested that V is generally small and of

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† Part XVI, S. F. Mason, B. J. Peart, and R. E. Waddell, preceding paper.

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

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

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

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

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uncertain sign, and that V is more reliably evaluated by comparing the absorption band frequency of a tris-chelate complex with that of the corresponding mono-chelate complex.[8-10]

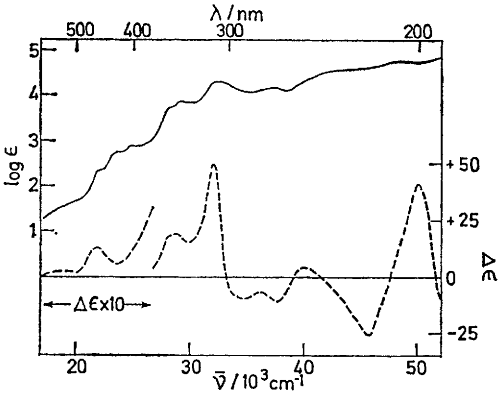

FIGURE 1 The absorption (upper curve) and circular dichroism spectrum (lower curve) of (+)-$[Cr(bipy)_3]^{3+}$ in water

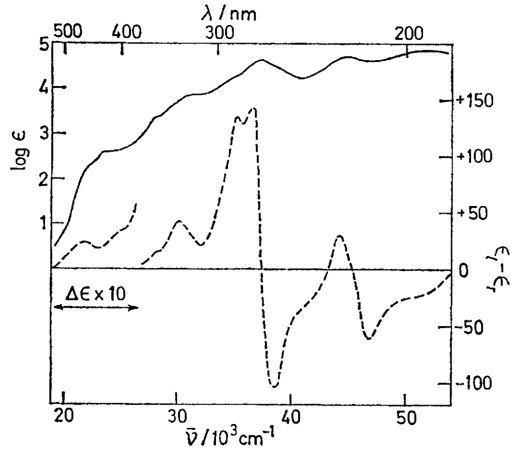

FIGURE 2 The absorption (upper curve) and c.d. spectrum (lower curve) of (+)-$[Cr(phen)_3]^{3+}$ in water

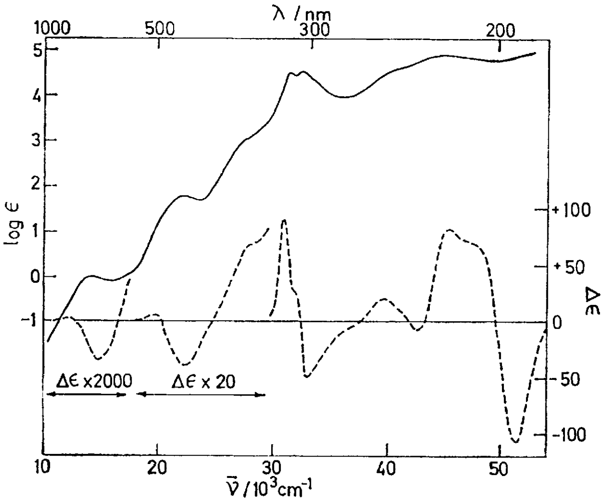

FIGURE 3 The absorption (upper curve) and c.d. spectrum (lower curve) of (+)-$[Co(bipy)_3]^{3+}$ in water

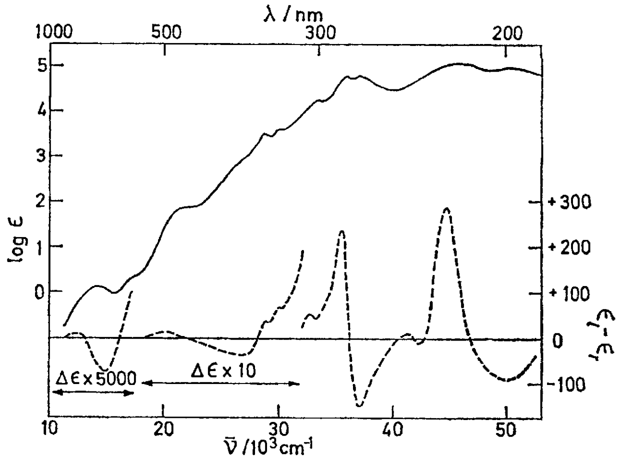

FIGURE 4 The absorption (upper curve) and c.d. spectrum (lower curve) of (+)-$[Co(phen)_3]^{3+}$ in water

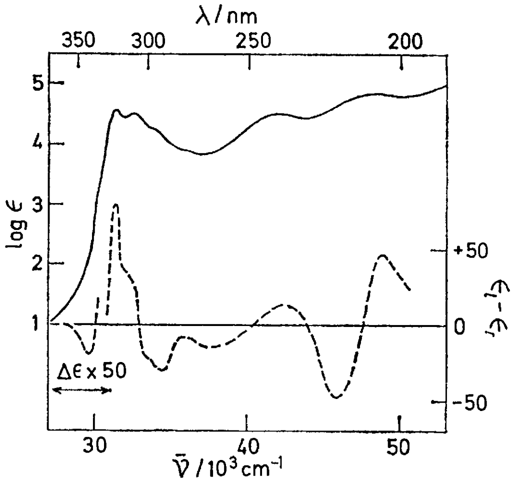

FIGURE 5 The absorption (upper curve) and c.d. spectrum (lower curve) of (+)-$[Rh(bipy)_3]^{3+}$ in water

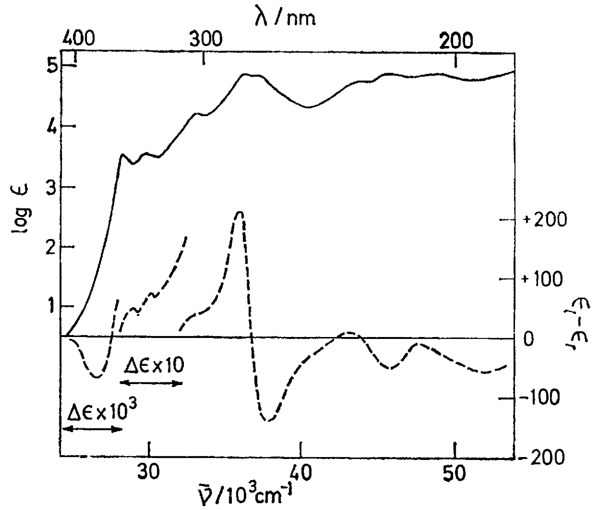

FIGURE 6 The absorption (upper curve) and c.d. spectrum (lower curve) of (+)-$[Rh(phen)_3]^{3+}$ in water

In order to examine the scope of the methods proposed[1,9] for determining the sign of V and of the

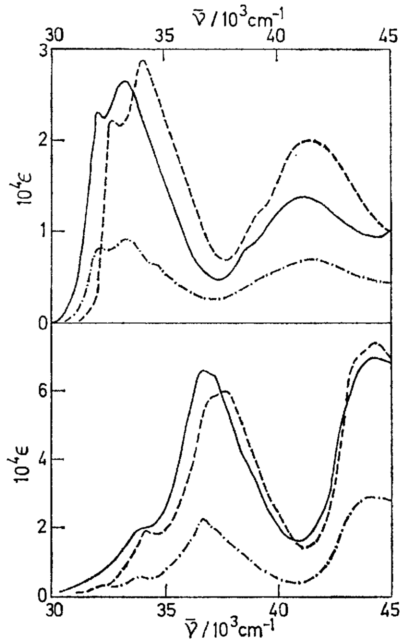

FIGURE 7 The absorption spectra of bipyridyl complexes (upper curves) and phenanthroline complexes (lower curves); $[In(L)_3]^{3+}$ (——), $[Cd(L)_3]^{2+}$ (– – – –), and $[Pb(L)]^{2+}$ (—·—·—)

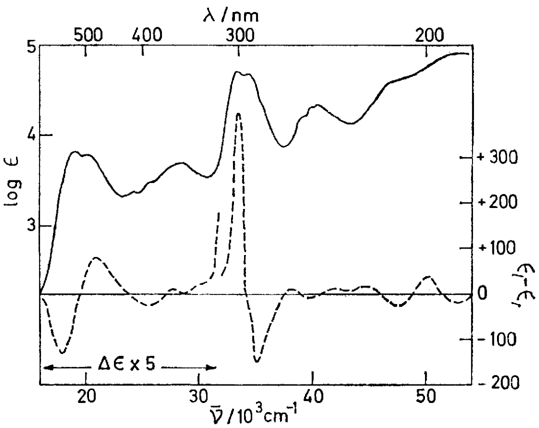

FIGURE 8 The absorption (upper curve) and c.d. spectrum (lower curve) of $(-)$-$[Fe(bipy)_3]^{2+}$ in water at 4°

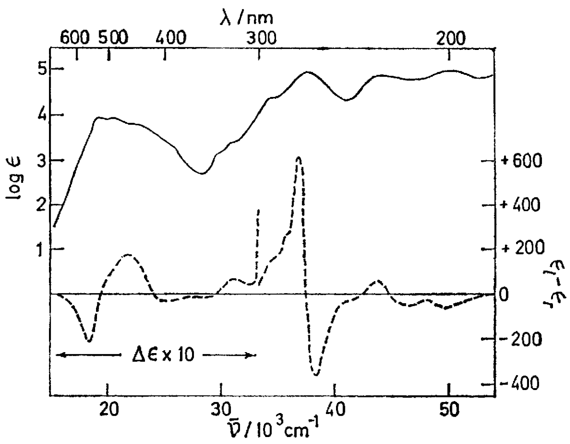

FIGURE 9 The absorption (upper curve) and c.d. spectrum (lower curve) of $(-)$-$[Fe(phen)_3]^{2+}$ in water at 4°

implications of the SCF calculations on the iron(II) complex,[3-7] we have measured, or remeasured over a more extended wavelength range under higher resolution, the absorption and c.d. spectra of the trisbipyridyl and trisphenanthroline complexes of chromium(III) (Figures 1 and 2), cobalt(III) (Figures 3 and 4), rhodium(III) (Figures 5 and 6), cadmium(II) and iridium(III) (Figure 7), iron(II) (Figures 8 and 9) and iron(III) (Figures 10 and 11), and other metals of the iron-group (Table), together with the bis-complexes, $(-)$-*cis*-$[Co(bipy)_2(NO_2)_2]^+$ (Figure 12) and $(+)$-$[Co(phen)_2(NO_2)_2]^+$ (Figure 13). The resolutions of $[Cr(bipy)_3]^{3+}$, $[Rh(bipy)_3]^{3+}$,

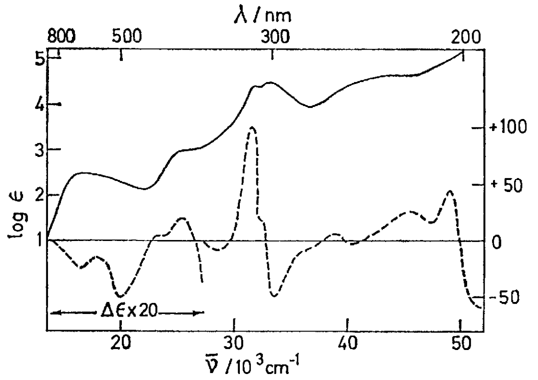

FIGURE 10 The absorption (upper curve) and c.d. spectrum (lower curve) of $(-)$-$[Fe(bipy)_3]^{3+}$ in water at 4°

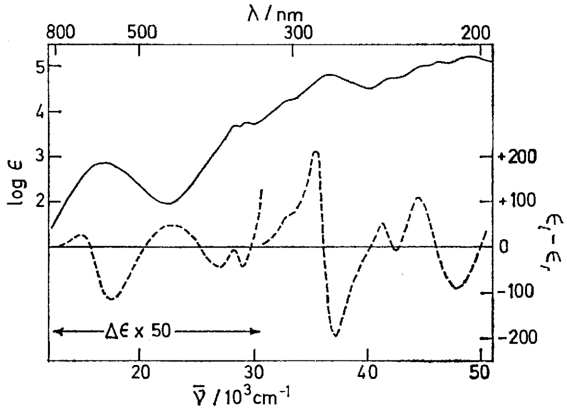

FIGURE 11 The absorption (upper curve) and c.d. spectrum (lower curve) of $(-)$-$[Fe(phen)_3]^{3+}$ in water at 4°

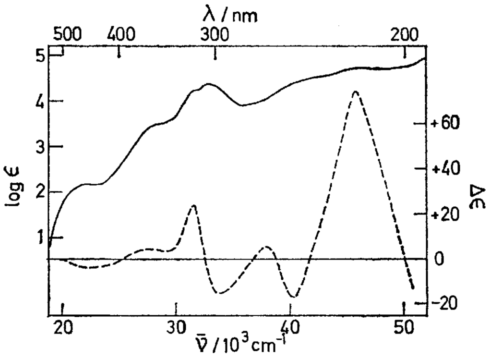

FIGURE 12 The absorption (upper curve) and c.d. spectrum (lower curve) of $(-)$-*cis*-$[Co(bipy)_2(NO_2)_2]^+$ in water

$[Rh(phen)_3]^{3+}$, *cis*-$[Co(bipy)_2(NO_2)_2]^+$, and *cis*-$[Co(phen)_2(NO_2)_2]^+$, which are new but almost certainly incomplete, were achieved with (—)-barium tris(catechyl)arsenate(V).[12-14]

The isomers which form the less-soluble (—)-$[As(cat)_3]^-$ salt, (+)-$[Cr(bipy)_3]^{3+}$, (+)-$Rh(phen)_3]^{3+}$, (+)-$[Rh(bipy)_3]^{3+}$, (—)-$[Co(bipy)_2(NO_2)_2]^+$, and (+)-$[Co(phen)_2(NO_2)_2]^+$, exhibit a common pattern of a major positive c.d. band at lower frequency and a negative c.d. band at higher frequency in the region of the lowest-energy ligand π-absorption with long-axis polarisation, like (+)-$[Ni(phen)_3]^{2+}$ and (+)-$[Fe(phen)_3]^{2+}$ (Table).

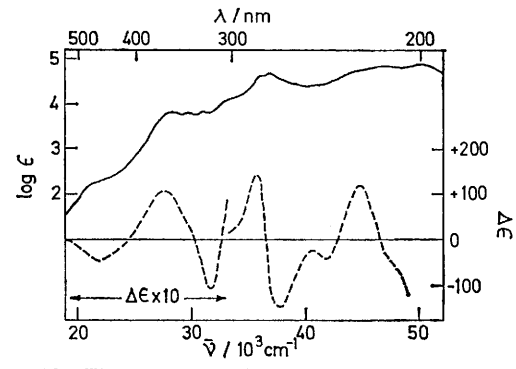

FIGURE 13 The absorption (upper curve) and c.d. spectrum (lower curve) of (+)-*cis*-$[Co(phen)_2(NO_2)_2]^+$

The absorption and circular dichroism spectra of bipyridyl and phenanthroline complexes in the region of the lowest-energy ligand excitation with long-axis polarisation

Complex	Circular dichroism: *E*-mode ν(kK)	Δε	*A*$_2$-mode ν(kK)	Δε	Absorption: (A_2 + *E*) modes ν(kK)	$10^3ε$	$[α]_D$
(+)-$[Ni(phen)_3]^{3+}$	36·5	+550	38·3	−260	36·9; 37·5	87	+1460
(—)-$[Fe(phen)_3]^{2+}$	36·8	+625	38·5	−360	37·5	89	−1400
(+)-$[Ru(phen)_3]^{2+}$	37·4	+540	38·9	−410	38·2	89	+1340
$(+)_{546}$-$[Os(phen)_3]^{2+}$	37·3	+470	39·0	−300	37·8	93	+3650 [c]
(—)-$[Fe(phen)_2]^{3+}$	35·5	+210	37·3	−190	36·4	71	−ve
(—)-$[Ru(phen)_3]^{3+}$	36·0	+415	38·0	−265	36·6	78	−580
$(+)_{546}$-$[Os(phen)_3]^{3+}$	35·9	+310	38·3	−150	36·5	66	+400 [c]
(+)-$[Cr(phen)_3]^{3+}$	36·5	+145	38·6	−105	37·3	44	+1200
(+)-$[Co(phen)_3]^{3+}$	35·3	+240	36·9	−150	35·7; 36·5	67	+800
(+)-$[Rh(phen)_3]^{3+}$	35·9	+215	37·7	−140	36·1; 36·6	71	+650
(+)-$[Co(phen)_2(NO_2)_2]^+$	35·7 [a]	+140	37·7 [b]	−145	35·7; 36·7	50	+760
$(+)_{546}$-$[Ni(bipy)_3]^{2+}$	32·5	+250	35·1	−50	32·6; 33·9	48	+500 [c]
(—)-$[Fe(bipy)_3]^{2+}$	33·3	+405	35·1	−150	33·4; 34·5	56	−4600
(+)-$[Ru(bipy)_3]^{2+}$	34·4	+240	36·1	−105	34·9	56	+800
$(+)_{546}$-$[Os(bipy)_3]^{2+}$	34·0	+320	35·7	−120	34·5	71	+4000 [c]
(—)-$[Fe(bipy)_3]^{3+}$	L.S	+100	33·3	−50	31·7; 32·9	31	−ve
(—)-$[Ru(bipy)_3]^{3+}$	31·6	+85	33·9	−35	31·8; 32·8	63	−400
$(+)_{546}$-$[Os(bipy)_3]^{3+}$	31·7	+160	35·3	−90	31·7; 32·6	31	+250 [c]
(+)-$[Cr(bipy)_3]^{3+}$	31·9	+50	34·5	−8	32·0	22	+600
(+)-$[Co(bipy)_3]^{3+}$	31·2	+90	33·2	−50	31·6; 32·8	35	+260
(+)-$[Rh(bipy)_3]^{3+}$	31·3	+80	34·4	−30	31·4; 32·6	38	+120
(—)-$[Co(bipy)_2(NO_2)_2]^+$	31·3 [a]	+25	33·8 [b]	−15	31·5; 32·8	24	−360

[a] *A*-Symmetry in C_2. [b] *B*-Symmetry in C_2. [c] At 546 nm.

The isomer[15] (—)-$[Fe(phen)_3]^{2+}$ and[16] (+)-$[Ni(phen)_3]^{2+}$ have been assigned to the Λ-configuration by the anomalous *X*-ray diffraction method, as well as the exciton c.d. procedure,[17] which indicates additionally, from the signs of the c.d. bands (Table), that the bipyridyl and phenanthroline complexes forming the less-soluble (—)-$[As(cat)_3]^-$ salt have the same Λ-configuration. Both the *X*-ray[18] and the c.d. method[18,19] give (—)-$[As(cat)_3]^-$ the Δ-configuration, so that the less-soluble salts studied contain a complex cation and complex anion with antipodal configurations. In contrast, the less-soluble salts formed by $[Ni(phen)_3]^{2+}$ and $[Co(ox)_3]^{3-}$ contain a complex cation and anion with the same configuration,[16] and the same holds for the less-soluble salts formed by $[Co(ox)_3]^{3-}$ with other trisphenanthroline and trisbipyridyl complexes,[1] illustrating the limitations of solubility methods for relating stereochemical configuration.

The extended absorption and c.d. spectrum of (—)-$[Fe(phen)_3]^{2+}$ (Figure 9) supports the SCF treatments[3-5] of this complex, particularly the more detailed calculation[5] in which interaction between 162 excited configurations was taken into account. The extended spectrum shows that there are no major c.d. bands in the 30—54 kK region of the ligand π-absorption other than the exciton pair centred at 37·5 kK (Figure 9). This pair of oppositely-signed c.d. bands, and the analogous pairs observed near 37 kK in other trisphenanthroline complexes (Table), were ascribed in our earlier work[1,2,17] to the Coulombic coupling of the *p*-band excitations of the three ligands. The *p*-band of phenanthroline arises from the out-of-phase combination of the long-axis polarised $\pi_7 \rightarrow \pi_8$ and $\pi_8 \rightarrow \pi_9$ one-electron excitations, the π-orbitals being

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[12] A. Rosenheim and W. Plato, *Chem. Ber.*, 1925, **58**, 2000.

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[15] D. H. Templeton, A. Zalkin, and T. Ueki, *Acta Cryst., Suppl.*, 1966, **A21**, 154.

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

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

numbered upwards from the most-bonding level, and on this basis the corresponding in-phase combination, giving the β′-band of phenanthroline is expected to give rise in a tris-complex to further major exciton c.d. bands in the frequency region now accessible. Such additional bands are not observed (Figure 9) and it is concluded, following the SCF studies,[3-5] that the 37 kK c.d. absorption of the trisphenanthroline complexes arises from the exciton coupling of the excitation giving the β′-band of the ligand. The *p*-band excitation is weak and is extensively mixed with charge-transfer excitations in the $[Fe(phen)_3]^{2+}$ complex.[5]

The extended spectra of (−)-$[Fe(bipy)_3]^{2+}$ show similarly that there are no further major c.d. bands in the 30—54 kK ligand absorption region beyond the exciton pair centred at 34 kK (Figure 8). The more detailed SCF treatment of this complex, covering interaction between 162 excited configurations,[7] supports our previous assignment [1] of the major c.d. bands near 34 kK to the Coulombic coupling of the *p*-band excitations ($\pi_6 \rightarrow \pi_7$) of the ligands. The β′-band excitations of the bipyridyl ligands, also long-axis polarised, are only weakly coupled in the tris-complex, and although the corresponding A_2 and E exciton modes have an appreciable rotational strength the energy-interval between the two modes is vanishingly small and little resultant c.d. absorption is expected.[7] The frequency-interval between the A_2 and E exciton states arising from the Coulombic coupling of the lowest-energy ligand excitation with long-axis polarisation in a tris-complex is expected to be relatively large, the calculated values of that interval [equation (1)] being +1100 cm^{-1} for [7] $[Fe(bipy)_3]^{2+}$ and +1400 cm^{-1} for [5] $[Fe(phen)_3]^{2+}$.

The extended spectra of the divalent iron-group metals [20] and of nickel(II) [21] show generally that there are no major c.d. bands in the 30—54 kK region except for the oppositely-signed exciton pair near 34 and 37 kK in the trisbipyridyl and trisphenanthroline complexes, respectively. The trivalent complexes commonly exhibit further c.d. bands of comparable magnitude (Figures 1, 3—5, and 10—13). As they are absent from the spectra of the divalent complexes, these additional c.d. bands are not due to internal ligand π-excitations and are attributed to metal–ligand charge-transfer configurations. A charge-transfer excitation in a trisbipyridyl or trisphenanthroline complex giving rise to substantial c.d. absorption is long-axis polarised with respect to each ligand, or has a major long-axis component. Such a charge-transfer excitation mixes with long-axis polarised internal-ligand π-excitations and, if of higher energy, as appears common in the case of the trivalent metal complexes, repels the latter excitations to lower energies, but, if of lower frequency, as in the case of the divalent iron-group complexes, repels the latter excitations to higher frequencies. Thus the absorption and the associated c.d. near 34 and 37 kK in the trisbipyridyl and trisphenanthroline complexes, respectively, is generally found at a lower frequency in the trivalent than the divalent metal complexes (Table). The trivalent trisphenanthroline complex with the highest absorption and c.d. frequencies near 37 kK is (+)-$[Cr(phen)_3]^{3+}$, which shows charge-transfer c.d. on the long-wavelength edge of the main exciton c.d. bands [11] (Figure 2), whereas the corresponding complex with the lowest absorption and c.d. frequencies near 37 kK is (+)-$[Co(phen)_3]^{3+}$, which exhibits major charge-transfer c.d. bands at 44·6 and 50 kK (Figure 4).

The frequency-difference between the corresponding absorption or c.d. bands of (+)-$[Cr(phen)_3]^{3+}$ and (+)-$[Co(phen)_3]^{3+}$ near 37 kK is greater than 1000 cm^{-1}, which is the order of the frequency-interval between the A_2 and E exciton states [equation (1)] resulting from the coupling of the 37 kK phenanthroline excitations. Thus the proposal,[8-10] that the sign and the magnitude of the exciton-splitting energy, V [equation (1)], is given by the frequency-shift of an absorption band between a mono-chelate and the corresponding tris-chelate complex, is not likely to be reliable, if only because of the interaction between charge-transfer and internal-ligand π-excitations prevalent in the bipyridyl and phenanthroline complexes.

Moreover, even in the absence of charge-transfer effects and of π-delocalisation between the ligands, the frequency-shift of the centre-of-gravity of absorption from a mono- to a tris-chelate complex does not measure the exciton-splitting energy, V [equation (1)]. If electron-exchange between the ligands in a tris-chelate complex is neglected, the energies of the transition from the ground to the A_2 and E exciton states of the complex are,[1]

$$\Delta E(A_2) = \Delta E^\circ + 2(U' - U) + 2V \qquad (2)$$

and

$$\Delta E(E) = \Delta E^\circ + 2(U' - U) - V \qquad (3)$$

where ΔE° is the corresponding excitation energy of the reference monomer, *e.g.* the mono-chelate complex, and the additional terms represent Coulombic interactions between two individual ligands in the tris-complex. The term, U, refers to the Coulombic potential between the stationary charge distribution in the ligand L_a and that of ligand L_b, both in the electronic ground state, whereas U' is the corresponding interaction when one ligand is in the excited and the other in the ground electronic state, and V represents the potential between the transitional charge distributions in the two ligands.

As the dipole-strength of the transition to the A_2 exciton state of a tris-chelate complex is twice as large as that of the transition to the E state, it is expected that the absorption shifts by V between the mono- and the tris-complex if the term $2(U' - U)$ common to equations (2) and (3) is neglected.[8-10] However, the general shift of both the A_2 and E transitions of a tris-complex, due to the neglected term $2(U' - U)$, may be larger than the splitting-energy, V, particularly when

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[20] B. J. Peart, Thesis, University of East Anglia, 1970.

[21] M. J. Harding, S. F. Mason, and B. J. Peart, Part XVIII, following paper.

the latter is small, as is suggested [8-10] for the case of the trisbipyridyl complexes. Thus the adoption of the band-shift criterion, advocated by Hawkins and his co-workers,[8-10] suggests that V is positive and large for $[Cd(phen)_3]^{2+}$ (+1000 cm^{-1}) and $[Cd(bipy)_3]^{2+}$ (+700 cm^{-1}) but negative and small (−100 cm^{-1}) for $[In(phen)_3]^{3+}$ and $[In(bipy)_3]^{3+}$ (Figure 7). A frequency-interval between the A_2 and E transitions [equation (1)] of 3 kK would result in resolved A_2 and E absorption bands or a much larger bandwidth than is observed for $[Cd(phen)_3]^{2+}$ (Figure 7). The red-shift of the absorption between the cadmium(II) and indium(III) tris-chelate complexes (Figure 7) probably arises from the common term $2(U' - U)$ of equations (2) and (3) which is expected to have a larger negative value for the smaller interligand separations obtaining in the indium(III) complexes.

The absorption band-shift criterion [8-10] is contraindicated not only by charge-transfer effects and the Coulombic term $2(U' - U)$ [equations (2) and (3)], which produce comparable shifts of both the A_2 and E transitions, but also by the differences between the types of excitation giving rise to circular dichroism and to isotropic absorption. The exciton circular dichroism arises only from long-axis polarised ligand π-excitations whereas the associated isotropic absorption may be due additionally to contributions from short-axis polarised excitations. The uniform and low degree of polarisation ($p = +0{\cdot}23$) observed [22] in the polarised fluorescence and excitation spectrum of phenanthroline over the 30—39 kK range suggests the presence of superposed long- and short-axis polarised electronic or vibronic transitions in the ligand over this range. Thus the use of absorption data for the assignment of c.d. bands requires caution and is contraindicated where other methods are available. For this reason our earliest criterion,[23] that the A_2 exciton c.d. band lies at a frequency closer to that of the absorption band maximum than the corresponding E exciton c.d. band, since the dipole strengths have the relative value, $D(A_2) = 2D(E)$, for long-axis polarised ligand excitations, is regarded as of limited reliability as the band-shift criterion.[8-10]

In the alternative approach [1,2] attention is directed primarily to the rotational strengths of the A_2 and E transitions resulting from the coupling of the long-axis polarised ligand π-excitations in a tris-chelate complex. The frequency-interval [equation (1)] between those rotational strengths is independent of any frequency-shift common to both transitions, due to the Coulombic term $2(U' - U)$ [equations (2) and (3)], and is not greatly affected by charge-transfer interactions.[1-7] Short-axis polarised excitations, close in energy and contributing to the isotropic absorption have a negligible effect upon the frequency-interval [equation (1)], for although the Coulombic matrix elements connecting configurations of E-symmetry derived from long- and short-axis polarised excitations do not generally vanish, as is assumed in some MO treatments of the iron(II) complexes,[3,6] those elements are very small.

The observed areas of the exciton c.d. bands of the trisbipyridyl and trisphenanthroline complexes, in the cases where optical purity is assured, correspond to some 40% of the theoretical rotational strengths calculated in the point-dipole approximation.[1,11] The loss of 60%, due to the overlap on the frequency-scale of oppositely-signed rotational strengths, is consistent with a frequency-interval [equation (1)] of some +1000 cm^{-1} on the assumption of a Gaussian band-shape. A similar interval is given by a vibronic analysis in the intermediate coupling exciton treatment,[11] and by the more-detailed of the SCF calculations on the iron(II) complexes.[5,7] These observations provide the basis for the conclusion that V is generally positive in the trisbipyridyl and trisphenanthroline series and that all of the chiral complexes listed (Table) have the Λ-configuration since, in all cases, the major exciton c.d. bands lie in order of positive and then negative to higher frequency.

EXPERIMENTAL

Materials.—Literature methods were used to prepare and resolve the trisphenanthroline complexes of nickel(II),[24] iron(II),[25] ruthenium(II),[26] osmium(II),[27] chromium(III),[28] and cobalt(III),[28] and the trisbipyridyl complexes of nickel(II),[29] iron(II),[30] ruthenium(II),[31] osmium(II),[32] and cobalt(III).[9] The optical isomers of the divalent iron-group complexes were oxidised to the corresponding trivalent isomers by the procedures of Dwyer and Gyarfas.[33] The iron(III) complexes were found to have an enhanced optical stability in strong acid solution (Figure 14).

The racemic complexes, $[Cr(bipy)_3]Cl_3$,[34] $[Rh(phen)_3]Cl_3$,[35] $[Co(phen)_2(NO_2)_2]Cl$,[36] and $[Co(bipy)_2(NO_2)_2]Cl$,[36] were partly resolved with $(-)$-$Ba[As(cat)_3]_2$.[12-14] A typical resolution of a tris-chelate complex was as follows. To $[Rh(phen)_3]Cl_3$ (0·30 g) in water (10 ml) was added $(-)$-$Ba[As(cat)_3]_2,2H_2O$ (0·29 g) in 50% aqueous acetone (10 ml). Acetone (30 ml) was added until the first-formed

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yellow precipitate dissolved, and the filtered solution was stored at 0° for several days. After removal of the solid, (+)-[Rh(phen)$_3$](−)[As(cat)$_3$]$_3$, water was added to the filtrate to precipitate more of this diastereoisomer. Addition of 0·1M-perchloric acid to the diastereoisomer racemised the (−)-[As(cat)$_3$]$^-$ ion in a few minutes,[14] leaving (+)-[Rh(phen)$_3$]$^{3+}$ as the sole optically-active species in solution. Aqueous solutions of (−)-[Rh(phen)$_3$]$^{3+}$ were obtained by the rotatory evaporation of acetone from the residual filtrates. The less-soluble diastereoisomers, (+)-[Rh(bipy$_3$](−)-[As(cat)$_3$]$_3$ and (+)-[Cr(bipy)$_3$](−)-[As(cat)$_3$]$_3$ were formed similarly but (+)-[Co(phen)$_2$(NO$_2$)$_2$](−)-[As(cat)$_3$] and (−)-[Co(bipy)$_2$-(NO$_2$)$_2$](−)-[As(cat)$_3$] were obtained as the less-soluble diastereoisomers from 1 : 4 water–acetonitrile solutions.

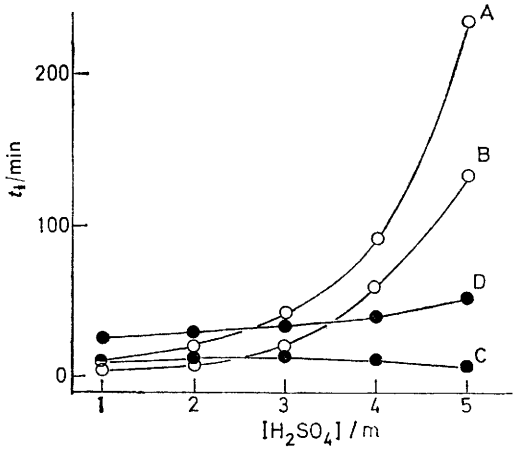

FIGURE 14 The half-life for racemisation, $t_{\frac{1}{2}}$ (min), as a function of sulphuric acid concentration, of A, (−)-[Fe(bipy)$_3$]$^{2+}$ and B, (−)-[Fe(phen)$_3$]$^{2+}$ at 24° and of C, (−)-[Fe(bipy)$_3$]$^{3+}$ and D, (−)-[Fe(phen)]$^{3+}$ at 2°

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 over the range 185—610 nm and with a laboratory-constructed instrument[37] at longer wavelengths. Short pathlengths (0·1 mm) and appropriately concentrated solutions were used to measure the spectra of the tris-chelate complexes of cadmium(II) and indium(III), in order to minimise the effects of dissociation. The c.d. spectra of the nickel(II), iron(II), and iron(III) complexes were obtained at 4° to minimise the effects of racemisation which were taken into account by extrapolation to the time of dissolution or, in the case of the iron(III) complexes, to the time of completion of oxidation.

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