Optical Rotatory Power of Co-ordination Compounds. Part XVIII.† The Circular Dichroism of Trigonal Nickel(II) Chelate Complexes

By **Michael J. Harding, Stephen F. Mason,*** and **Barry J. Peart,** School of Chemical Sciences, University of East Anglia, Norwich, and Chemistry Department, King's College, Strand, London WC2R 2LS

The axial circular dichroism spectrum of $[Ni(en)_3]^{2+}$ in the hexagonal host crystal, $[Zn(en)_3](NO_3)_2,6H_2O$, has been measured, together with the solution c.d. spectra of tris-1,2-diamine and tris-1,2-di-imine complexes of nickel(II). The results show that the spin-allowed octahedral transition of nickel(II) with the lowest energy, $^3A_{2g} \rightarrow {}^3T_{2g}$, is allowed for magnetic dipole radiation and breaks down in tris-1,2-diamine complexes with the Δ-configuration into a lower-energy doubly-degenerate component with a negative rotational strength and a higher-energy non-degenerate component with a positive rotational strength, like the corresponding transition in the analogous complexes of d^3 and low-spin d^6 transition-metal ions. The similarities between the d^3, d^6, and d^8 cases are found to extend to the c.d. absorption of the second d-electron transition and of the u.v. charge-transfer transition. The complex $[Ni(tren\text{-}py_3)]^{2+}$ {tren-py$_3$ = tris-[4-(2-pyridyl)-3-azabut-3-enyl]amine} has been resolved and the Δ-configuration is tentatively assigned to the (−)-isomer from its c.d. spectrum.

THE optical activity of trigonal complexes containing metal ions with the d^3 or low-spin d^6 configuration has been studied more extensively than that of other tris-chelate complexes as the latter in general are optically the less stable.[1-7] These studies have been directed towards spectroscopic and stereochemical applications, notably, the empirical[8] or theoretically-based[9] correlation of the absolute configuration of a complex with the sign of a circular dichroism absorption due to an identified electronic transition and, more recently, the development of sector rules relating the optical activity of a complex to the disposition of substituents in the chiral molecular environment of the symmetric chromophore.[10,11]

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

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In the present work we report an analogous investigation of trigonal nickel(II) complexes. Although kinetically labile, the tris-chelate complexes of nickel(II) with 1,2-diamines and α-amino-acids are thermodynamically stable and do not dissociate appreciably in aqueous solution at room temperature,[12] while the 1,2-di-imine complexes have an optical stability [13,14] adequate for solution c.d. measurements. Owing to the equatorial preference of the methyl group with respect to the mean plane of the chelate ring, (—)-propylenediamine forms a tris-complex, $[\mathrm{Ni}(l\text{-pn})_3]^{2+}$, with the Δ-configuration [15] and the *lel*-conformation,[16] in which the carbon–carbon bond of each chelate ring is nearly parallel to the three-fold rotation axis of the complex, or with the Λ-configuration [15] and the *ob*-conformation,[16] in which the ring carbon–carbon bonds are obliquely inclined with respect to that axis. The *lel*-conformation has the lower energy,[16] and, in the case of $[\mathrm{Co}(l\text{-pn})_3]^{3+}$, only 15% of the *ob*-form is present in solution under equilibrium conditions.[17] A similar conformational ratio probably obtains in the case of $[\mathrm{Ni}(l\text{-pn})_3]^{2+}$ and the corresponding (—)-*trans*-cyclohexane-1,2-diamine complex, $[\mathrm{Ni}(l\text{-chxn})_3]^{2+}$. It is assumed here, as in previous work on [5,6] $[\mathrm{Ni}(l\text{-pn})_3]^{2+}$ and [18] $[\mathrm{Ni}(l\text{-chxn})_3]^{2+}$, that the c.d. spectra of these complexes (Figures 1—3) refer predominantly to the Δ-configuration and *lel*-conformation (Δλλλ). The same configurational assignments are adopted on the basis of stereospecific co-ordination, and are extended to the tris-L-proline complex of nickel(II), in a recent discussion [19] of the *d*-electron optical activity of tris-chelate complexes of nickel(II).

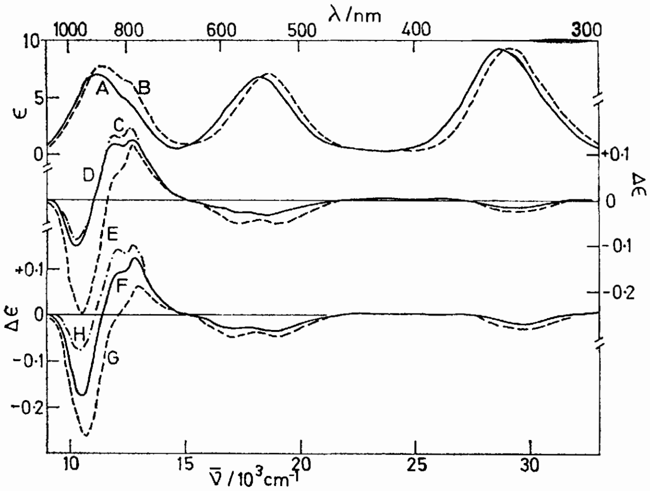

FIGURE 1 The absorption spectrum of $[\mathrm{Ni}(l\text{-pn})_3]\mathrm{Cl}_2,2\mathrm{H}_2\mathrm{O}$ (A) in water and (B) in methanol and the circular dichroism spectrum of (C) $[\mathrm{Ni}(l\text{-pn})_3]\mathrm{SO}_4$ in 0·5M-aqueous $\mathrm{Na}_2\mathrm{SO}_4$ and of $[\mathrm{Ni}(l\text{-pn})_3]\mathrm{Cl}_2,2\mathrm{H}_2\mathrm{O}$ in (D) water, (E) dimethyl sulphoxide, (F) methanol, (G) 2M-methanolic LiCl, and (H) of $[\mathrm{Ni}(l\text{-pn})_3](\mathrm{BPh}_4)_2$ in methanol

The isomers $(+)$-$[\mathrm{Ni}(\mathrm{bipy})_3]^{2+}$ and $(+)$-$[\mathrm{Ni}(\mathrm{phen})_3]^{2+}$ have been assigned [20] to the Λ-configuration from the signs and the frequency-order of the two major c.d. bands arising from the Coulombic coupling of the long-axis polarised excitations of 2,2′-bipyridyl and 1,10-phenanthroline near 33 and 37 kK, respectively (Figures

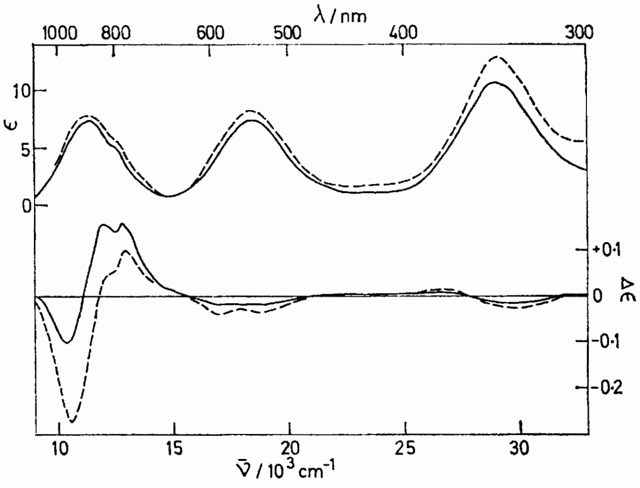

FIGURE 2 The absorption spectra (upper curves) and circular dichroism (lower curves) of $[\mathrm{Ni}(l\text{-chxn})_3]\mathrm{Cl}_2,3\mathrm{H}_2\mathrm{O}$ in water (——) and in methanol (– – – –)

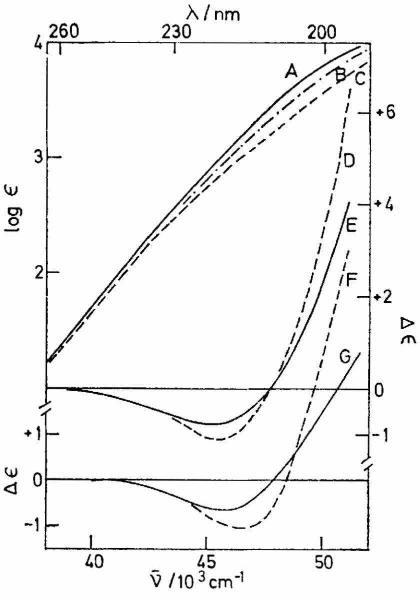

FIGURE 3 The absorption spectra (A) of $[\mathrm{Ni}(l\text{-chxn})_3]\mathrm{Cl}_2,3\mathrm{H}_2\mathrm{O}$ in water, and of $[\mathrm{Ni}(l\text{-pn})_3]\mathrm{Cl}_2,2\mathrm{H}_2\mathrm{O}$ (B) in methanol and (C) in water, and the circular dichroism of $[\mathrm{Ni}(l\text{-chxn})_3]\mathrm{Cl}_2,3\mathrm{H}_2\mathrm{O}$ (D) in methanol and (E) in water, and of $[\mathrm{Ni}(l\text{-pn})_3]\mathrm{Cl},2\mathrm{H}_2\mathrm{O}$ (F) in methanol and (G) in water

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4 and 5). A recent X-ray diffraction study[21] confirms that (+)-$[Ni(phen)_2]^{2+}$ has the Λ-configuration. The corresponding exciton c.d. absorption of a third 1,2-di-imine complex, (—)-$[Ni(tren\text{-}py_3)]^{2+}$, is not sufficiently well-defined to allow a firm assignment of configuration (Figure 6). The ligand, tren-py_3 {tris-[4-(2-pyridyl)-3-azabut-3-enyl]amine} is the heptadentate Schiff base formed[22] by the condensation of pyridine-2-carbaldehyde with 2,2,2-triaminoethylamine (tren).

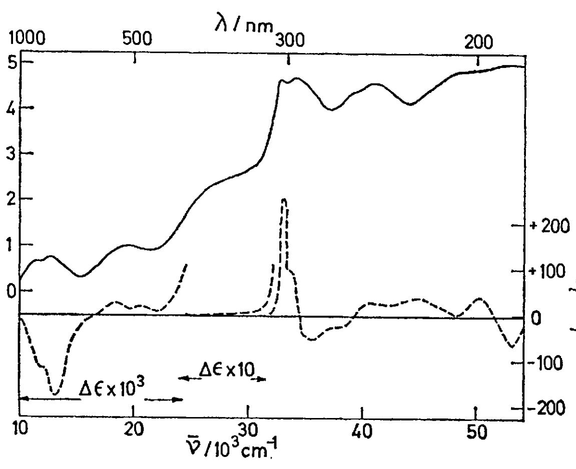

FIGURE 4 The absorption spectrum (upper curve) and circular dichroism (lower curve) of (+)-$[Ni(bipy)_3](ClO_4)_2$ in water

The correlation of the stereochemical configuration of a chiral nickel(II) complex with the sign of a Cotton effect with a known origin requires methods for identifying the particular electronic transition responsible for a given c.d. absorption. Four methods are available from previous studies.[8,23] First,[8] the axial c.d. spectrum of a single uniaxial crystal containing a trigonal complex orientated with its threefold rotation axis parallel to the crystal axis records solely the optical activity of electronic transitions polarised perpendicular to that axis with E-symmetry in the group D_3 or C_3. Secondly, the relative frequencies and, thirdly, the relative intensities of the plane-polarised absorption of a trigonal complex orientated in a single crystal, whether uniaxial or not, correlate with the relative positions and magnitudes of the bands in the corresponding c.d. spectrum.[8] Fourthly, environmental effects distinguish between c.d. bands arising from transitions with different symmetries.[23] Where feasible, each of these methods has been employed in the present work.

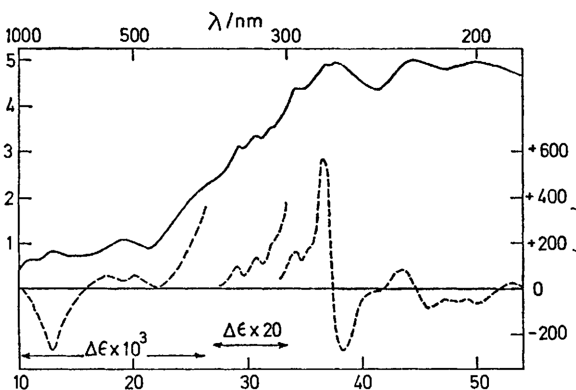

FIGURE 5 The absorption spectrum (upper curve) and circular dichroism (lower curve) of (+)-$[Ni(phen)_3](ClO_4)_2$ in water

Although the trisethylenediamine complex of nickel(II) is optically too labile to be resolved, the hexagonal crystal, $[Ni(en)_3](NO_3)_2,6H_2O$, consists of domains which each contain one of the optical isomers.[24] The $[Ni(en)_3]^{2+}$ ion substitutes into the analogous hexagonal crystal,[25] $[Zn(en)_3](NO_3)_2,6H_2O$, and the axial circular dichroism spectrum of a doped crystal indicates that only one optical isomer of the nickel complex is present in any given yrcstal (Figure 7). Positive- and negative-rotating crystals were obtained statistically, but the magnitude of the c.d. absorption was constant to within 10%. At room temperature the magnitude of the dipole and rotational strength of the $[Ni(en)_3]^{2+}$ ion in the crystal over the region of the octahedral ${}^3A_{2g}\rightarrow{}^3T_{2g}$ absorption centred at 11·3 kK is 183×10^{-40} and 12×10^{-40} c.g.s. units, respectively, giving a dissymmetry factor or g-value of 0·27. The corresponding absorption of the tetragonal optically-active crystal, $[Ni(H_2O)_6]SO_4$, has a g-value[26] of 0·24 and that of the analogous ${}^1A_{1g}\rightarrow{}^1T_{1g}$ absorption of the hexagonal crystal, (+)-$[Co(en)_3Cl_3]_2,NaCl,6H_2O$, is[27] 0·245. From the similar values of these g-factors it is concluded that the $[Ni(en)_3]^{2+}$ ions substituted into a given crystal of $[Zn(en)_3](NO_3)_2,6H_2O$ have the same configuration and

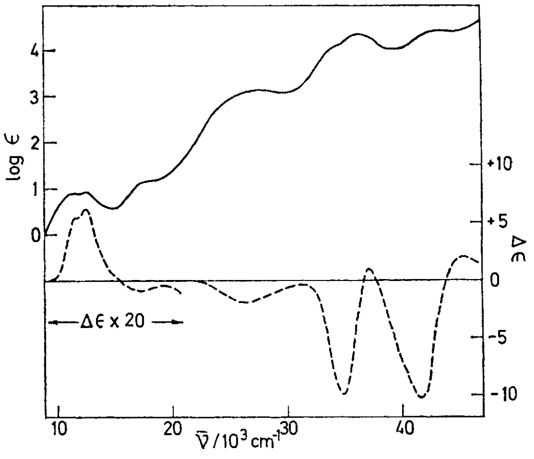

FIGURE 6 The absorption spectrum (upper curve) and circular dichroism (lower curve) of (—)-$[Ni(tren\text{-}py_3)](ClO_4)_2$ in water

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that the C_3 axis of each $[Ni(en)_3]^{2+}$ ion is parallel to the optic axis of the crystal.

The two absorption and c.d. bands observed at 11·3 and 18·4 kK in the axial crystal spectrum (Figure 7) refer to the E-components in D_3 of the octahedral nickel(II) d-electron transitions from the $^3A_{2g}$ ground state to the $^3T_{2g}$ and $^3T_{1g}(F)$ excited state, respectively. The third spin-allowed d-electron transition to the $^3T_{1g}(P)$ excited state, observed near 29 kK in the solution spectra of $[Ni(l\text{-pn})_3]^{2+}$ (Figure 1) and $[Ni(l\text{-chxn})_3]^{2+}$ (Figure 2), is obscured in the crystal spectrum of $[Ni(en)_3]^{2+}$ by the onset of absorption due to the nitrate ion. The rotational strength of the axial crystal c.d. band at 11·3 kK, $R(E,T_2)$ is some 30 times larger than that, $R(E,T_1)$, of the 18 kK c.d. band (Figure 7), supporting the expectation that the octahedral transitions of nickel(II), $^3A_{2g}\rightarrow{}^3T_{2g}$ and $^3A_{2g}\rightarrow{}^3T_{1g}(F)$, are respectively allowed and forbidden for magnetic-dipole radiation. Whereas $R(E,T_2)$ represents the scalar product of a zero-order magnetic moment and a first-order electric moment due to the perturbation of the trigonal field in the $[Ni(en)_3]^{2+}$ ion, $R(E,T_1)$ is first order in both moments and thus second order overall.

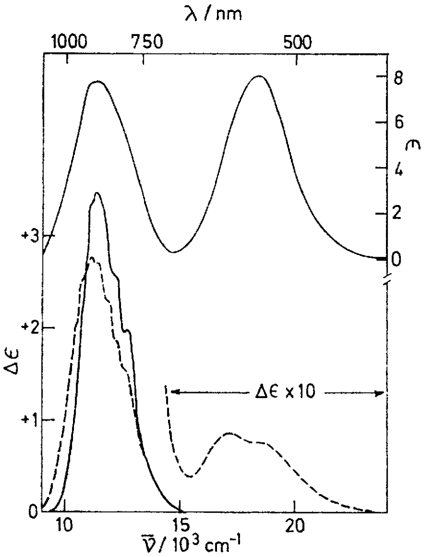

FIGURE 7 The axial single crystal absorption spectrum of $[Ni(en)_3]^{2+}$ in the host lattice of $[Zn(en)_3](NO_3)_2,6H_2O$ (upper curve) and the corresponding circular dichroism (lower curves) at room temperature (– – – –) and 80 K (——).

The crystal c.d. band at 11·3 kK shows a vibronic structure with a prominent interval of ~300 cm^{-1} which probably represents an upper-state totally-symmetric nickel–nitrogen stretching mode. At 80 K the low-frequency band-edge shifts to the blue, owing to the elimination of the hot bands, but the vibronic structure is not appreciably sharpened (Figure 7). The interval of 1500 cm^{-1} observed in the crystal c.d. band at 18 kK is too large to represent a vibrational mode or first-order spin-orbit coupling (Figure 7). The first-order spin-orbit splitting of the $^3T_{1g}(F)$ state of $[Ni(NH_3)_6]^{2+}$ is estimated[28] to be some 600 cm^{-1}, and there are no singlet states close enough in energy to give rise to strong second-order spin-orbit interaction. A possible origin of the interval and the analogous separation of 2000 cm^{-1} observed in the corresponding c.d. band of $[Ni(l\text{-pn})_3]^{2+}$ (Figure 1), $[Ni(l\text{-chxn})_3]^{2+}$ (Figure 2), (+)-$[Ni(bipy)_3]^{2+}$ (Figure 4), and (+)-$[Ni(phen)_3]^{2+}$ (Figure 5), is the Jahn–Teller distortion of an excited E-electronic state by an e_g vibrational mode.[29] The $^5T_{2g}\rightarrow{}^5E_g$ transition of iron(II) substituted in a $KMgF_3$ crystal gives a split absorption at 9 kK with an interval of 1350 cm^{-1} which is attributed[30] to such a Jahn–Teller distortion.

A comparison of the axial crystal spectrum of $[Ni(en)_3]^{2+}$ (Figure 7) with the solution spectra of $[Ni(l\text{-pn})_3]^{2+}$ (Figure 1) and $[Ni(l\text{-pn})_3]^{2+}$ (Figure 2) shows that $R(E,T_1)$ near 18 kK has a similar magnitude in all three complexes, allowing for a reduction by a factor of (2/3) in the latter two cases, due to the random orientation of the complex ions in solution, and a further minor reduction due to the small fraction of Λ-ob-forms. It is inferred that the $^3A_2\rightarrow{}^3A_2$ trigonal component of the octahedral transition to the $^3T_{1g}(F)$ state is optically-inactive, in conformity with the D_3 selection rules. The lower-energy crystal c.d. band at 11·3 kK (Figure 7) is, however, an order of magnitude larger than the corresponding solution c.d. absorption (Figures 1 and 2), showing that $R(A_1,T_2)$ has a similar magnitude and opposed sign to $R(E,T_2)$. The band areas of $R(A_1,T_2)$ and $R(E,T_2)$ overlap and mutually cancel to within some 90% for the complex ions randomly oriented in solution, leaving a residual band-wing c.d. absorption over the 8—15 kK region (Figures 1 and 2).

The crystal spectrum of $[Ni(en)_3]^{2+}$ indicates that $R(E,T_2)$ and $R(E,T_1)$ have the same sign (Figure 7), and the negative c.d. bands of $[Ni(l\text{-pn})_3]^{2+}$ (Figure 1) and $[Ni(l\text{-chxn})_3]^{2+}$ (Figure 2) at 10·5 and 18 kK are accordingly assigned to the trigonal components, $^3A_2\rightarrow{}^3E$, of the transitions to the octahedral states, $^3T_{2g}(F)$ and $^3T_{1g}(F)$, respectively. The positive c.d. band at 12 kK arises from the $^3A_2\rightarrow{}^3A_1(^3T_{2g})$ trigonal component which is close in energy and mixes through second-order spin-orbit coupling[31,32] with the spin-forbidden, $^3A_2\rightarrow{}^1E(^1D)$, transition, appearing in absorption and c.d. near 12·8 kK (Figures 1 and 2). The absorption intensity of the $^3A_2\rightarrow{}^1E(^1D)$ transition in a crystal of $[Ni(en)_3](NO_3)_2,6H_2O$ is larger for radiation polarised parallel than polarised perpendicular to the C_3 axis of the complex ion,[33] indicating that the $^3A_2\rightarrow{}^3A_1(^3T_{2g})$ trigonal component is the major source of the borrowed intensity.

The energy-interval between the $^3A_1$ and ^3E trigonal components of the octahedral $^3T_{2g}$ state in a tris-diamine

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[33] R. Dingle and R. A. Palmer, *Theor. Chim. Acta*, 1966, **6**, 249.

nickel(II) complex, $[\bar{\nu}(A_1) - \bar{\nu}(E)]$, is estimated to be $+100$ cm^{-1} from the axial crystal and solution c.d. spectra (Figures 1, 2, and 7). No splitting between these two trigonal components was detected in the polarised crystal spectrum of $[Ni(en)_3](NO_3)_2,6H_2O$, but oscillator-strengths of 9·0 and 8·0 $\times 10^{-5}$ were reported [33] for the transitions to the $^3A_1$ and ^3E components of the octahedral $^3T_{2g}$ state. The corresponding absorption of $[Ni(NH_3)_6]^{2+}$ has an oscillator strength [34] of 5·3 $\times 10^{-5}$ so that the first-order increments to the oscillator strength due to the trigonal field in $[Ni(en)_3]^{2+}$ lie in the ratio, $f(A_1) : f(E) = 1{\cdot}4 : 1$. This ratio is expected to have the value of 2·0 if $R(A_1,T_2)$ and $R(E,T_2)$ have the same magnitude and the lower value observed suggests that the major of the two c.d. bands observed in the solution spectra over the 8—15 kK region (Figures 1 and 2) arises from the $^3A_2 \rightarrow {}^3E(^3T_{2g})$ transition. The negative c.d. band at 10·5 kK (Figures 1 and 2) assigned to that transition from the axial crystal c.d. spectrum (Figure 7) has the major band area only in nonaqueous solvents, and both the criteria for identifying the origin of c.d. bands from the corresponding plane-polarised crystal spectrum are found to be of limited application in the present case.

A similar conclusion emerges from studies of the 1,2-di-imine complexes of nickel(II). A polarised spectrum of racemic $[Ni(bipy)_3]^{2+}$ substituted into the monoclinic crystal, $[Zn(bipy)_3]SO_4,7H_2O$, gives [35] the intensity ratio, $I(A_1) : I(E) = 0{\cdot}7 : 1$, for the trigonal components of the octahedral transition to the $^3T_{2g}(F)$ state of the complex. This ratio might be taken to imply that the negative c.d. band of (+)-$[Ni(bipy)_3]^{2+}$ and (+)-$[Ni(phen)_3]^{2+}$ at 13 kK is due to the $^3A_2 \rightarrow {}^3E(^3T_{2g})$ component (Figures 4 and 5). However, these two isomers have the Λ-configuration,[20, 21] whereas a negative $R(E,T_2)$ correlates with the Δ-configuration for $[Ni(l\text{-pn})_3]^{2+}$ and $[Ni(l\text{-chxn})_3]^{2+}$ (Figures 1, 2, and 7). Attempts to adopt the basic method of measuring the axial crystal c.d. spectrum, by substituting (+)- or (−)-$[Ni(bipy)_3]^{2+}$ into the hexagonal crystal,[35] $[Zn(bipy)_3]Br_2,6H_2O$, were frustrated by the rapid racemisation of the optical isomer and the limited optical quality of the doped crystals.

The contrary assignment of the negative c.d. band of (+)-$[Ni(bipy)_3]^{2+}$ and (+)-$[Ni(phen)_3]^{2+}$ at 13 kK to the $^3A_2 \rightarrow {}^3A_1(^3T_{2g})$ component gives the following consistencies with the corresponding tris-diamine spectra. First, the effects of a change from water to a nonaqueous solvent are similar, reducing $R(A_1,T_2)$ and enhancing $R(E,T_2)$ (Figures 1, 2, and 8). In aqueous acetone solution (+)-$[Ni(phen)_3]^{2+}$ gives a negative c.d. band of diminished area at 13 kK and a positive band appears at 10·7 kK which is ascribed to the $^3A_2 \rightarrow {}^3E(^3T_{2g})$ component (Figure 8). Secondly, $R(E,T_1)$ and $R(E,T_2)$ have the same sign in both the tris-1,2-diamine and the tris-1,2-di-imine series (Figures 1, 2, 4, 5, 7, and 8). Thirdly, $R(E,T_2)$ lies at a lower frequency than $R(A_1,T_2)$ and it is positive for the Λ-configuration, which is in agreement with the generalisation for the tris-1,2-diamine [8] and tris-1,2-di-imine [20] complexes of transition metal ions with the d^3 or low-spin d^6 configuration that the rotational strength of the doubly degenerate component of the lowest energy octahedral d-electron transition lies at a lower frequency than the corresponding non-degenerate component and is positive for the Λ-configuration.

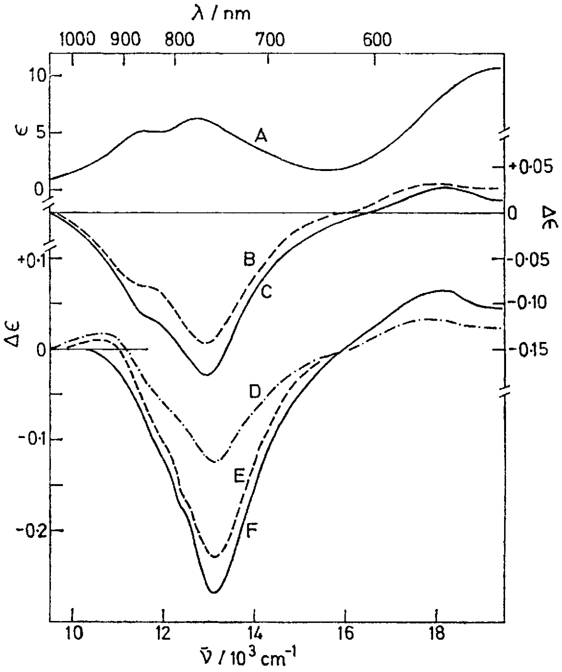

FIGURE 8 The absorption spectrum (A) of $[Ni(bipy)_3]^{2+}$ in water and the circular dichroism of (+)-$[Ni(bipy)_3]^{2+}$ (B) in 50% aqueous acetone and (C) in water, and of (+)-$[Ni(phen)_3]^{2+}$ (D) in 50% aqueous acetone, (E) in 1·0M-aqueous sodium selenite and (F) in water

The effect of polarisable counterions on the c.d. spectra of the nickel(II) complexes studied is not uniform and does not give the spectroscopic application found [23] in the corresponding cobalt(III) series. Sulphate and thiosulphate enhance $R(A_1,T_2)$ and diminish $R(E,T_2)$, while the halides in nonaqueous solution produce the contrary effect upon the c.d. spectrum of $[Ni(l\text{-pn})_3]^{2+}$ in the 8—15 kK region (Figure 1), similar to the results obtained [23] for the corresponding bands of tris-diamine complexes with d^3 and low-spin d^6 metal ions. However, selenite produces a small diminution of both c.d band areas in the 8—15 kK region of the spectrum of $[Ni(l\text{-pn})_3]^{2+}$ but gives rise to the positive 10·7 kK c.d. band of (+)-$[Ni(phen)_3]^{2+}$ accompanied by a reduction of the negative 13 kK c.d. band area (Figure 8).

The analogies between the c.d. absorption of the tris-1,2-diamine complexes of nickel(II) and of metal ions with the d^3 or low-spin d^6 configuration extend to the higher-energy bands of the spectrum. The c.d. band at 18 kK in the nickel(II) series, representing $R(E,T_1)$, is negative for the Δ-configuration (Figures 1 and 2) and positive for the Λ-configuration (Figures 4 and 5), and

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[35] R. A. Palmer and T. S. Piper, *Inorg. Chem.*, 1966, **5**, 864.

the same rule holds for the corresponding band of the tris-1,2-diamine complexes of chromium(III), cobalt(III), and rhodium(III) with the *lel*-conformation.[8,36] Similarly the c.d. associated with the allowed ligand–metal charge-transfer transition, which has a maximum[36] near 47 kK in the tris-diamine complexes of cobalt(III) but a frequency higher than 52 kK in the corresponding complexes of nickel(II) (Figure 3), is positive for the Δ-configuration, or negative for the Λ-configuration.

Although designed as a potentially heptadentate ligand giving capped octahedral metal complexes with C_{3v} symmetry, tris-[4-(2-pyridyl)-3-azabut-3-enyl]amine forms an octahedral nickel(II) complex,[22] $[\mathrm{Ni(tren\text{-}py_3)}]^{2+}$. The three imine and the three pyridine nitrogen atoms are disposed approximately at the apices of a regular octahedron with a nickel–nitrogen bond distance of 2·10 Å whereas the seventh donor atom, the tertiary nitrogen of the 2,2,2-triaminotriethylamine moiety, lies at a distance of 3·25 Å from the metal ion.[22,37] The complex $[\mathrm{Ni(tren\text{-}py_3)}]^{2+}$, having C_3 symmetry, is chiral and a resolution has been achieved with antimonyl-(+)-tartrate which forms the less-soluble salt with (−)-$[\mathrm{Ni(tren\text{-}py_3)}]^{2+}$. The isomers of $[\mathrm{Ni(tren\text{-}py_3)}]^{2+}$ are optically more stable than those[13] of $\mathrm{Ni(phen)_3]^{2+}$ or of[14] $[\mathrm{Ni(bipy)_3}]^{2+}$, having a half-life of 43 h for racemisation in aqueous solution at room temperature.

The absorption and c.d. spectrum of (−)-$[\mathrm{Ni(tren\text{-}py_3)}]^{2+}$ (Figure 6) are similar in form to those of (+)-$[\mathrm{Ni(phen)_3}]^{2+}$ and (+)-$[\mathrm{Ni(bipy)_3}]^{2+}$ (Figures 4 and 5) but the c.d. absorption in the 30—50 kK region of the ligand π-electron transitions is substantially weaker. As the ligands have C_{2v} symmetry, the π-electron excitation moments of 2,2′-bipyridyl or 1,10-phenanthroline in a tris-chelate complex lie either along the octahedral edge, spanned by the chelate ring or along the C_2 axis of the complex passing through that ring. The moments directed along octahedral edges couple to give the two major exciton c.d. bands of opposite sign observed near 34 kK in (+)-$[\mathrm{Ni(bipy)_3}]^{2+}$ (Figure 4) or near 37 kK in (+)-$[\mathrm{Ni(phen)_3}]^{2+}$ (Figure 5). Since the lower-energy exciton c.d. band, due to the degenerate *E*-coupling mode, is positive and the higher-energy c.d. band, due to the A_2-coupling mode, is negative (Figures 4 and 5) both (+)-$[\mathrm{Ni(bipy)_3}]^{2+}$ and (+)-$[\mathrm{Ni(phen)_3}]^{2+}$ have the Λ-configuration.[9,20] The 2-iminopyridine chromophore has only a plane of symmetry and the π-electron excitation moments of this ligand in a tris-complex have a general orientation in the plane defined by the octahedral edge spanned by the ligand and the normal from the metal ion to that edge. Whatever the orientation of the moments, with the particular exception of direction along the normals, it is expected that the three isoenergetic π-excitation moments of the ligands in a tris(2-iminopyridine) complex with C_3 symmetry couple to give a lower-energy negative exciton c.d. band, due to the *E*-coupling mode, and a higher-energy positive c.d. band, due to the *A*-coupling mode, for the Δ-configuration. As the two c.d. bands associated with both the 36 and the 43 kK absorption of (−)-$[\mathrm{Ni(tren\text{-}py_3)}]^{2+}$ follow this pattern (Figure 6) the isomer is tentatively assigned to the Δ-configuration. The assignment is tentative since the c.d. observed in the 30—50 kK region is relatively small (Figures 4—6) and may arise from mechanisms other than interligand exciton coupling, *e.g.* from the coupling of ligand π-excitations with charge-transfer or metal-ion *d*-electron excitations. However, the *d*-electron optical activity has a similar magnitude but is enantiomeric in sign to that of (+)-$[\mathrm{Ni(bipy)_3}]^{2+}$ and (+)-$[\mathrm{Ni(phen)_3}]^{2+}$ (Figures 4—6), supporting the tentative assignment of the Δ-configuration to (−)-$[\mathrm{Ni(tren\text{-}py_3)}]^{2+}$.

EXPERIMENTAL

Materials.—Standard methods were used to obtain (−)-propylenediamine,[17] (−)-*trans*-cyclohexane-1,2-diamine,[38] $[\mathrm{Ni(\mathit{l}\text{-}pn)_3]Cl_2,2H_2O}$,[39] $[\mathrm{Ni(\mathit{l}\text{-}chxn)_3]Cl_2,3H_2O}$,[18] (+)-$[\mathrm{Ni(bipy)_3](ClO_4)_2}$,[14] and (+)-$[\mathrm{Ni(phen)_3](ClO_4)_2}$.[13]

The preparation described[22] for $[\mathrm{Ni(tren\text{-}py_3)](PF_6)_2}$ was adapted to obtain $[\mathrm{Ni(tren\text{-}py_3)](ClO_4)_2}$ (Found: C, 42·7; H, 4·25; N, 14·4. Calc. for C, 42·95; H, 4·05; N, 14·6). Fractional recrystallisation of the antimonyl-(+)-tartrate by the method described[40] for the resolution of $[\mathrm{Cr(phen)_3}]^{3+}$ gave a less-soluble diastereoisomer, $[\alpha]_D$ −180°, which was converted into the perchlorate, (−)-$[\mathrm{Ni(tren\text{-}py_3)](ClO_4)_2}$ $[\alpha]_D$ −236°.

$[\mathrm{Ni/Zn(en)_3](NO_3)_2,6H_2O}$ *Crystals.*—These were grown as hexagonal needles up to 3 × 3 × 15 mm by the slow evaporation at room temperature of aqueous solutions containing stoicheiometric quantities of ethylenediamine and metal nitrates with zinc/nickel molar ratios of 10 and 50. Sections perpendicular to the hexagonal *c*-axis of the crystal were sawn off with wet cotton thread and polished first with moist filter paper and then with a lens cloth. With the polarising microscope, these sections showed no linear birefringence and gave an optical rotation invariant with respect to the rotation of the microscope stage. Conoscopic examination of the sections gave uniaxial interference figures. These crystal sections were used for c.d. measurements. Other sections, cut parallel to the *c*-axis of the crystal, showed marked linear birefringence, and gave linear dichroism spectra similar to those previously reported[25,33] for the orientated $[\mathrm{Ni(en)_3}]^{2+}$ ion. The concentration of nickel ions in a particular sample was obtained from a solution spectrophotometrically after a density determination of the crystal by the volume displacement method.

Spectra.—Absorption spectra were obtained with a Unicam SP 700 and a Cary 14 spectrophotometer. Optical rotations were measured with a Perkin-Elmer 141 polarimeter. Circular dichroism spectra were measured with a Jouan Dichrograph CD185 over the range 185—610 nm and with laboratory-constructed instruments[41] at longer wavelengths.

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