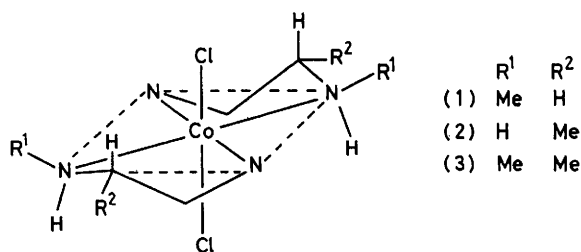


Influence of *N*-Alkyl Substituents in a Diamine Chelate Ring on the Optical Activity of the $[\text{Co}^{\text{III}}\text{N}_6]$ Chromophore

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The complexes $[\text{Co}(\text{diamine})(\text{en})_2]^{3+}$ (en = ethylenediamine; diamine = *N*-methyl-, *NN'*-dimethyl-, or *N*-isopropyl-ethylenediamine) have been obtained and resolved into optical isomers in order to investigate the effect of *N*-alkyl groups on the *d*-electron optical activity of the cobalt(III) tris(diamine) complexes. As in other types of complex containing the octahedral $[\text{Co}^{\text{III}}\text{N}_6]$ chromophore, the influence of *N*-alkyl groups is not large, in contrast to the major chiroptical effects produced by *N*-methyl substitution in chiral complexes containing the tetragonal $[\text{Co}^{\text{III}}\text{N}_4\text{Cl}_2]$ chromophore. A ligand-polarisation model for *d*-electron optical activity is used to show that, while the changes in the rotational strengths of the individual components of the ${}^1A_1 \rightarrow {}^1T_1$ octahedral *d*-electron transition produced by *N*-alkyl substitution are large, these changes mutually cancel when summed over the three components. The effects of *C*-alkyl substitution are small, either for the individual components or in sum.

THE *d*-electron optical activity of chiral cobalt(III) complexes containing a tetragonal chromophore, notably $[\text{Co}^{\text{III}}\text{N}_4\text{Cl}_2]$, and five-membered diamine chelate rings, is sensitive to the alkylation of a nitrogen atom, but not of a carbon atom, of the chelate rings.¹ Crystal-structure determinations by *X*-ray diffraction methods show that the *N*-methylethylenediamine complex,² $[\text{Co}(\text{Me-en})_2\text{Cl}_2]^+$ (1), and the (*S*)(+)-propylenediamine complex,³ $[\text{Co}\{(S)\text{pn}\}_2\text{Cl}_2]^+$ (2), have the same absolute configuration with a common δ conformation of the chelate rings, yet the circular dichroism (c.d.) spectra of complexes (1) and (2) over the



400–700 nm region are virtually enantiomorphous.¹ Over the same range, which covers the absorption region of the tetragonal components of the octahedral ${}^1A_1 \rightarrow {}^1T_1$ transition, the c.d. spectrum of complex (2) is similarly enantiomorphous to that of the analogue obtained from either *N*¹-methyl- or *N*²-methyl-(*S*)(+)-propylenediamine,⁴ e.g. $[\text{Co}\{N^1\text{Me-(S)pn}\}_2\text{Cl}_2]^+$ (3), where again the

chelate rings adopt the δ conformation. The c.d. spectra of the complexes (1) and (3) are similar, however, indicating that the effect of the *C*-methyl group of the latter complex on the *d*-electron optical activity is small.

The chiroptical effects of *N*-alkyl and *C*-alkyl substitution in a five-membered diamine chelate ring of a chiral tetragonal complex are rationalised by a hexadecadal sector rule which relates the sign of the Cotton effect due to a particular component of the ${}^1A_1 \rightarrow {}^1T_1$ *d*-electron transition of octahedral Co^{III} to the position of substituent groups in the co-ordinate frame of the chromophore.¹ The hexadecadal rule is supported by recent c.d. studies⁵ of the *NN'*-dimethylethylenediamine complexes $[\text{Co}(\text{Me}_2\text{-en})_2\text{Cl}_2]^+$ and $[\text{Co}(\text{en})(\text{Me}_2\text{-en})\text{Cl}_2]^+$. The intensities of the visible c.d. bands of the latter complexes and of (1)–(3) and $[\text{Co}\{N^2\text{Me-(S)pn}\}_2\text{Cl}_2]^+$ conform to an additive scheme, based on the hexadecadal rule, in which the contribution of an N-CH₃ group is relatively large while those of a CH-CH₃ group and a ring CH₂ group are equated and are relatively small.⁵

In contrast, an *N*-methyl group substituted into a five-membered diamine chelate ring has little or no effect on the visible c.d. spectrum of mono- or bis-diamine complexes containing the octahedral $[\text{Co}^{\text{III}}\text{N}_6]$ chromophore, notably those of the series⁴ $[\text{Co}(\text{NH}_3)_4(\text{diamine})]^{3+}$ (4)–(6) and $[\text{Co}(\text{NH}_3)_2(\text{diamine})_2]^{3+}$ (7)–(9), where the diamine is (*S*)(+)-propylenediamine or its *N*¹-methyl or *N*²-methyl derivative (Figure 1). The contrast is

* Y. Saito and H. Iwasaki, *Bull. Chem. Soc. Japan*, 1962, **35**, 1131.

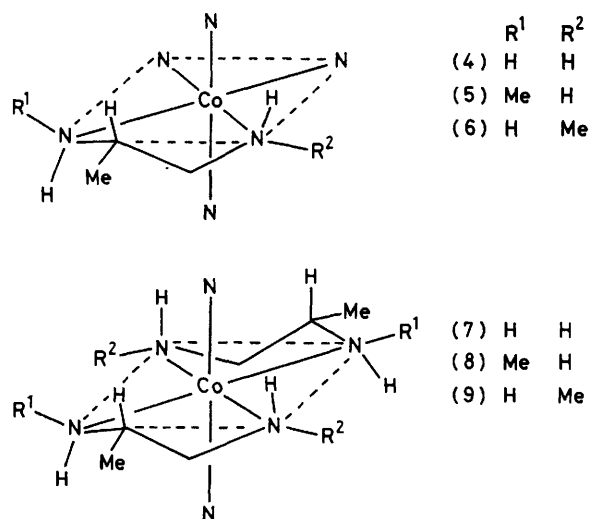
⁴ M. Saburi, Y. Tsujito, and S. Yoshikawa, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 203; *Inorg. Chem.*, 1970, **9**, 1476.

⁵ J. A. Tiethof and D. W. Cooke, *Inorg. Chem.*, 1972, **11**, 315.

¹ S. F. Mason, *J. Chem. Soc. (A)*, 1971, 667.

² W. T. Robinson, D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *Chem. Comm.*, 1969, 539.

rationalised by a sector rule restricted to chiral complexes containing an octahedral chromophore, in which the nodal surfaces are formed by the symmetry planes of the



octahedron.¹ The *N*-methyl group or groups of the complexes (5), (6), (8), and (9) lie in or close to a nodal surface of the octahedral sector rule. This surface is one of the four σ_d planes of the octahedron which are lost on descent in symmetry to D_{4h} and it is no longer a node of

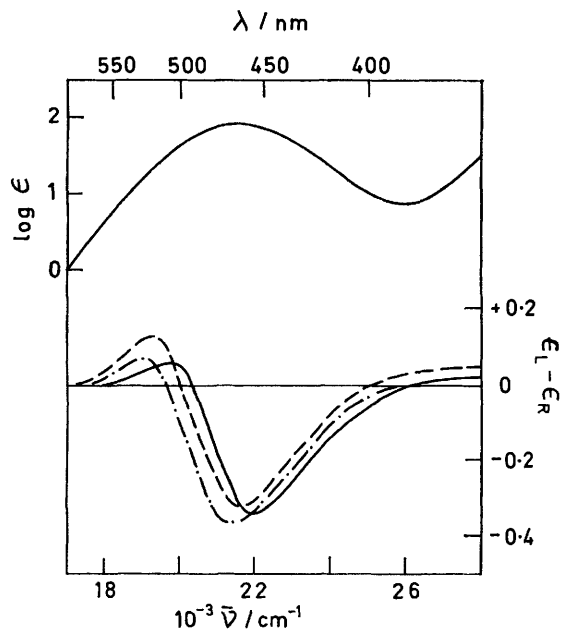


FIGURE 1 Absorption spectrum (upper curve) and c.d. spectra (lower curves) of (—) $[\text{Co}(\text{NH}_3)_4(\text{S})\text{pn}]^{3+}$ (4), (---) the N^1 -methyl derivative (5), and (-·-·-) the N^2 -methyl derivative (6) (adapted from ref. 4)

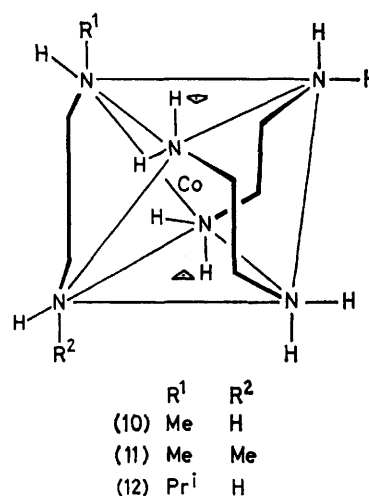
the hexadecadal regional rule, in which the sector-bounding surfaces are formed by the D_{4h} symmetry planes. In the hexadecadal sectors the *N*-methyl

⁶ S. F. Mason and R. H. Seal, *Mol. Phys.*, 1976, **31**, 755.

⁷ Y. Saito, *Co-ordination Chem. Rev.*, 1974, **13**, 305.

groups of complexes (1) and (3) have an antinodal location.¹

While the sector rules rationalise the c.d. data, they do not provide a physical basis for the relation between the *d*-electron optical activity of chiral cobalt(III) complexes and the location and properties of substituent groups. In the present work a ligand-polarisation model, developed for the treatment of the optical activity exhibited by cobalt(III) complexes derived from diamines containing primary amino-groups,⁶ is extended to investigate the chiroptical effect of the *N*-methyl group in a diamine chelate ring. In addition tris(diamine) complexes of Co^{III} containing *N*-alkyl- or *NN'*-dialkyl-ethylenediamine have been prepared and resolved, and c.d. spectra are reported for the isomers (+)[$\text{Co}(\text{en})_2(\text{Me-en})$]³⁺ (10), (+)[$\text{Co}(\text{en})_2(\text{Me}_2\text{-en})$]³⁺ (11), and (+)-[$\text{Co}(\text{en})_2(\text{Pr}^1\text{-en})$]³⁺ (12) ($\text{Pr}^1\text{-en}$ = *N*-isopropylethylenediamine) (Figure 2).



RESULTS AND DISCUSSION

Hitherto the main chiral complexes available containing the octahedral $[\text{Co}^{\text{III}}\text{N}_6]$ chromophore and *N*-alkyl-diamine chelate rings have been the mono- and *trans*-bis-diamine types, e.g. (5), (6), (8), and (9), in which the *d*-electron optical activity arises from a puckered chiral conformation of the puckered chelate ring or rings. In the corresponding tris(diamine) complexes optical activity is due additionally to the left-handed (Λ) or right-handed (Δ) screw configuration of the mean planes of the three chelate rings around the metal ion, and the effects of an *N*-alkyl group in a diamine chelate ring on the configurational and the conformational optical activity are not necessarily identical.

Furthermore, two types of puckering in the five-membered diamine chelate rings of cobalt(III) complexes are evident from the extensive X-ray crystal-structure analyses of Saito⁷ (Figure 3). In the thermodynamically more stable⁸ *lel* isomers of $[\text{Co}(\text{diamine})_3]^{3+}$, where the C-C bond of each chelate ring is parallel, or nearly so, to

⁸ E. J. Corey and J. C. Bailar, *J. Amer. Chem. Soc.*, 1959, **81**, 2620.

the three-fold rotation axis C_3 of the complex, each NH_2 group and the CH_2 group to which it is bonded are displaced in the same direction normal to the adjacent σ_h plane of the octahedron. In the corresponding *ob* isomer,

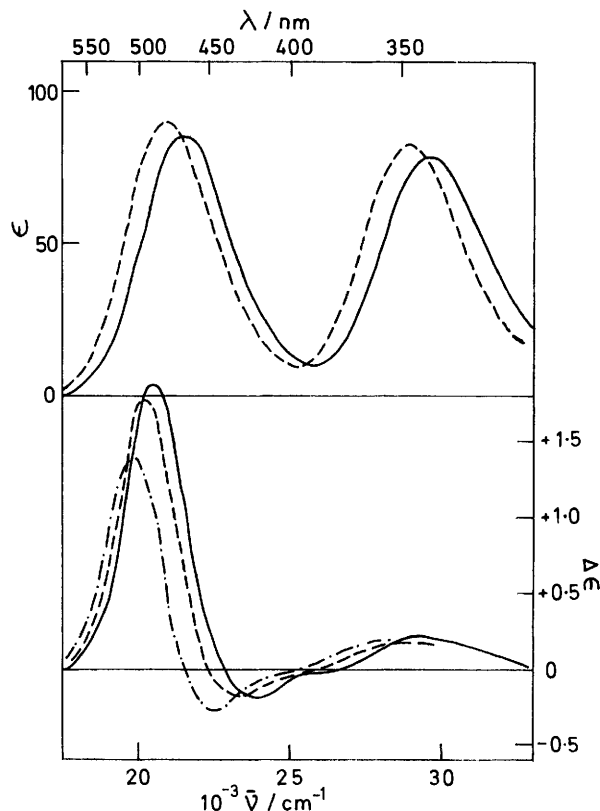


FIGURE 2 Absorption spectra (upper curves) and c.d. spectra (lower curves) of (—) $\Lambda(+)[\text{Co}(\text{en})_3]^{3+}$, (---) the *N*-methyl derivative (10), and (-·-·-) the *N*-isopropyl derivative (12) in water

where the C-C bond of each chelate ring is obliquely inclined with respect to the C_3 axis, each NH_2 group and the CH_2 group to which it is attached are displaced in opposite directions normal to the adjacent σ_h plane of the octahedron (Figure 3). The chiroptical effects of an *N*-alkyl group in a diamine chelate ring of the *lel* type and of the *ob* type again are not necessarily identical.

The crystal structure of *trans*-(—)[Co{(R)pn}₂Cl₂]-Cl·HCl·2H₂O determined by X-ray diffraction methods shows³ that the displacements of the groups forming the chelate rings from the adjacent σ_h plane are of the *ob* type, and it is probable that the corresponding displacements in the related *trans*-bis(diamine) complexes (7)—(9) are of the same type. The analogies between the c.d. spectra of (+)[Co(en)₃]³⁺ and of the tris(*N*-alkyldiamine)cobalt(III) complexes studied (Figure 2) indicate that (10)—(12) have the same Λ configuration as (+)[Co(en)₃]³⁺ and that *lel* conformations of the chelate rings similarly predominate in aqueous solution at ambient temperature, *i.e.* the forms $\delta\delta\delta$ and $\delta\delta\lambda$. Whether the chelate rings are of the *ob* or the *lel* type (Figure 3) the effect of *N*-alkyl substitution on the optical activity due to the ${}^1A_1 \rightarrow {}^1T_1$

transition of the octahedral [Co^{III}N₆] chromophore is not large (Figures 1 and 2), in contrast to the large chiroptical effects ensuing from the corresponding substitution in the *trans*-bis(diamine) complexes containing the tetragonal *trans*-[Co^{III}N₄Cl₂] chromophore.¹⁻⁵

The small overall influence of an *N*-alkyl group on the optical activity of a chiral complex containing the octahedral [Co^{III}N₆] chromophore is ascribed by the ligand-polarisation model to the mutual cancellation of relatively large rotational strengths of opposite sign induced by the *N*-alkyl group in the three degenerate components of the ${}^1A_1 \rightarrow {}^1T_1$ octahedral cobalt(III) transition (Table 1). When the degeneracy of that transition is broken, as in chiral complexes containing the tetragonal *trans*-[Co^{III}N₄Cl₂] chromophore, these rotational strengths, although necessarily modified by the change of chromophore, appear at different frequencies and no longer mutually cancel.

The ligand-polarisation treatment taken to the first order of perturbation theory refers the *d*-electron optical activity of a chiral diamine complex to the coupling of induced electric-dipole moments in the various groups of the chelate ring or rings with the intrinsic magnetic-dipole moment of the *d*-electron transition in the metal

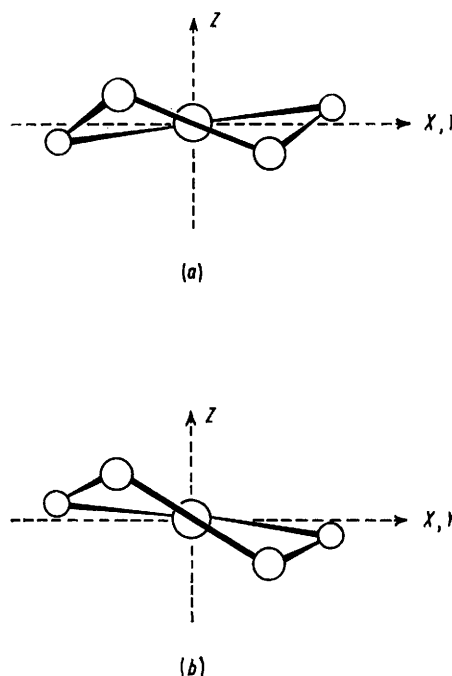


FIGURE 3 Distortions from the octahedral σ_h plane of the ligand groups in a 1,2-diamine chelate ring with the δ conformation observed (a) in an *ob*-tris(diamine) or a *trans*-bis(diamine) complex, and (b) in a *lel*-tris(diamine) complex

ion through the leading electric multipole of the transition⁶ (Figure 4). The ${}^1A_1 \rightarrow {}^1T_1$ transition of the octahedral [Co^{III}N₆] chromophore near 470 nm involves the *d*-orbital promotion, $d_{xy} \rightarrow d_{x^2-y^2}$, and the degenerate analogues, given by the cyclic permutation of the electronic co-ordinates. The leading transition moments of

the component $d_{xy} \rightarrow d_{x^2-y^2}$ are the z component of a magnetic dipole, m_z , and the $xy(x^2 - y^2)$ component of an electric hexadecapole, $H_{xy(x^2-y^2)}$.

Induced electric-dipole moments in the CH_2 and other groups of the chelate ring or rings, taken to be proportional to the mean polarisability of the ligand group,

TABLE I

Contribution of each group of a chelate ring formed by *N*-methylethylenediamine and by (*S*)(+)-propylenediamine in a complex containing the $[\text{Co}^{\text{III}}\text{N}_6]$ chromophore to the rotational strength R (10^{-40} c.g.s. units) of each component of the ${}^1A_1 \rightarrow {}^1T_1$ octahedral transition. The data refer in each case to the δ -ring conformation

<i>ob</i> - δ -Me-en	NH_2	CH_2	CH_3	NH	CH_3	Total
R^z	+2.50	-2.97	-2.97	+2.21	+9.74	+8.51
R^y	0	-1.03	+3.87	-2.21	-9.84	-9.21
R^x	-2.50	+3.87	-1.03	0	+0.13	+0.47
Sum	0	-0.13	-0.13	0	+0.03	-0.23
<i>lel</i> - δ -Me-en						
R^z	-0.57	-3.79	-3.79	-0.50	+10.56	+1.91
R^y	0	-1.38	+5.00	+0.50	-10.26	-6.14
R^x	+0.57	+5.00	-1.38	0	-0.37	+3.82
Sum	0	-0.17	-0.17	0	-0.07	-0.41
<i>ob</i> -(<i>S</i>)pn	NH_2	CH	CH_3	CH_2	NH_2	Total
R^z	+0.93	-2.33	-0.03	-2.96	+0.14	-4.25
R^y	0	-0.84	+0.04	+3.84	-0.14	+2.89
R^x	-0.93	+3.06	-0.01	-1.00	0	+1.13
Sum	0	-0.11	0	-0.12	0	-0.23
<i>lel</i> -(<i>S</i>)pn						
R^z	-0.57	-2.46	+0.03	-3.61	-0.87	-7.48
R^y	0	-0.91	0	+4.56	+0.87	+4.52
R^x	+0.57	+3.26	-0.03	-1.09	0	+2.71
Sum	0	-0.11	0	-0.14	0	-0.25

$\bar{\alpha}(\text{L})$, are correlated coulombically by the hexadecapolar transitional charge distribution. The resultant of the correlated electric-dipole moments has a component collinear with the magnetic-dipole moment of the d -electron transition in chiral complexes, e.g. a z component for the excitation to the configuration $\chi_{xy}^{x^2-y^2}$ in the octahedral $[\text{Co}^{\text{III}}\text{N}_6]$ chromophore (Figure 4). This component excitation has the rotational strength (1),⁶

$$R_{\text{oa}}^z = im_{\text{ao}}^z H_{\text{oa}}^{xy(x^2-y^2)} \sum_{\text{L}} \bar{\alpha}(\text{L}) G_{xy(x^2-y^2),z}^{\text{L}} \quad (1)$$

the sum being taken over the ligand groups L of the chelate rings.

If the transitional charge distribution of the component excitation, $\sum_i e_i x_i y_i (x_i^2 - y_i^2)$, is taken as a point hexadecapole at the metal-ion origin, the angular and radial geometric term in equation (1) governing the potential between this 2^4 -pole and the z component of a point electric dipole in the ligand group L situated at the position X, Y, Z in the octahedral frame (Figure 4) at a distance R from the metal ion is given by (2). The

$$G_{xy(x^2-y^2),z} = 315 XYZ (Y^2 - X^2) / 2R^{11} \quad (2)$$

rotational strengths of the other two components of the ${}^1A_1 \rightarrow {}^1T_1$ transition, due to excitations to the $\chi_{yz}^{y^2-z^2}$ and the $\chi_{zx}^{z^2-x^2}$ configuration in the octahedral $[\text{Co}^{\text{III}}\text{N}_6]$ chromophore, are obtained by cyclic permutation of the

co-ordinates in equations (1) and (2). The permutations show that, in the point-multipole approximation, the net first-order rotational strength of the ${}^1A_1 \rightarrow {}^1T_1$ transition sums to zero over the three components as in (3).

$$R({}^1T_1) = \sum_{\alpha=x,y,z} R_{\text{oa}}^{\alpha} = 0 \quad (3)$$

The point-multipole approximation is satisfactory only when the distance R between the multipoles is large relative to their individual dimensions. The radial factor for the 2^4 -pole moment of a $3d$ -electron transition is $\langle 3d | r^4 | 3d \rangle$ and double-exponent $3d$ wavefunctions⁹ give $[\langle r^4 \rangle]^{\ddagger}$ the values of 0.684 and 0.956 Å for Co^{3+} and neutral cobalt, respectively. Such a distance is not negligible relative to the metal-carbon distance (3 Å) in $[\text{Co}(\text{en})_3]^{3+}$, and a less approximate estimate of the potential between the 2^4 -pole moment of the metal ion

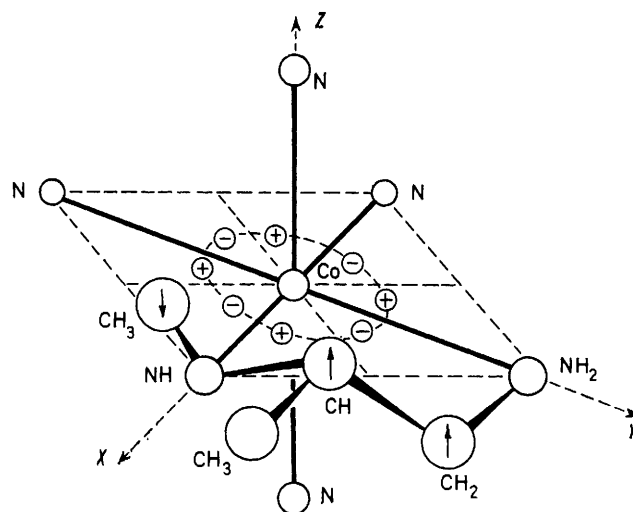


FIGURE 4 Correlation between the electric hexadecapole moment of the $d_{xy} \rightarrow d_{x^2-y^2}$ transition of the $[\text{Co}^{\text{III}}\text{N}_6]$ chromophore and the transient electric dipole induced in each ligand group of a 1,2-diamine chelate ring in the δ -conformation with an *N*-methyl and a *C*-methyl substituent, i.e. *N*¹-methyl-(*S*)(+)-propylenediamine

and the dipole of the ligand group is afforded by allowing the hexadecapole a radial extension within the limiting values calculated for Co^{3+} and neutral cobalt.

For computational purposes the 2^4 -pole moment of the $d_{xy} \rightarrow d_{x^2-y^2}$ excitation was taken to consist of eight point charges $\pm 2^{\frac{1}{2}}e/4$ disposed in the XY plane of the $[\text{Co}^{\text{III}}\text{N}_6]$ chromophore (Figure 4) at the maxima and minima of the angular-distribution function $[xy(x^2 - y^2)/r^4]$ and at a radial distance of 0.837 Å, corresponding to the value of $[\langle r^4 \rangle]^{\ddagger}$ for cobalt carrying a $+1.3e$ charge. The latter value allows for the partial neutralisation of the charge of Co^{III} due to the co-ordination of the lone-pair electrons of six amino-groups. The transitional charge distribution adopted (Figure 4) allows for the displacement of the charge $e/4$ in each quadrant of the XY plane in the one-electron excitation, $d_{xy} \rightarrow d_{x^2-y^2}$, and the factor of $2^{\frac{1}{2}}$

⁹ J. W. Richardson, W. C. Nieuvoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, 1962, **36**, 1057.

accommodates the promotion of either of the two electrons in the d_{xy} orbital in the ground state.

With a hexadecapole of finite dimensions the product of the 2^4 -pole transition moment and the geometric term governing the potential at a particular ligand-group point dipole in equation (1) becomes a sum over the monopolar transition charges, $q_{\text{oa}}^j = \pm 2^4 e/4$, as in (4)

$$S_z^L = \sum_{j=1}^8 q_{\text{oa}}^j Z_{jL} / R_{jL}^3 \equiv H_{\text{oa}}^{xy(x^2-y^2)} G_{xy(x^2-y^2),z}^L \quad (4)$$

where R_{jL} , with the components X_{jL} , Y_{jL} , and Z_{jL} , is the position vector of the ligand atom or group L with respect to the monopolar transition charge, q_{oa}^j , of the metal ion. The combination of equations (1) and (4) gives the z component of the transition ${}^1A_1 \rightarrow {}^1T_1$, in the $[\text{Co}^{\text{III}}\text{N}_6]$ chromophore with effective O symmetry, the first-order rotational strength (5). The rotational strengths of the

$$R_{\text{oa}}^z = im_{\text{ao}}^z \sum_L \bar{\alpha}(L) S_z^L \quad (5)$$

other two components, R_{oa}^x and R_{oa}^y , arising from excitations to the configurations $\chi_{yz}^{y^2-z^2}$ and $\chi_{zx}^{z^2-x^2}$ respectively are obtained from equation (5) by permuting the co-ordinates cyclically.

Computations based on equation (5) and its analogues were carried out for the complexes $[\text{Co}(\text{NH}_3)_4(\text{diamine})\delta]^{3+}$ where the diamine is either (S)(+)-propylenediamine or *N*-methylethylenediamine with a δ conformation and, in each case, displacements of the groups forming the chelate ring from the adjacent σ_h XY plane of both the *lel* and the *ob* type (Figure 3) were investigated (Table 1). The mean polarisability values adopted¹⁰ were 1.435, 1.84, and 2.24 Å³ for the CH, CH₂, and CH₃ group, respectively. As the mean polarisability of ammonia is reduced from 2.23 to 1.71 Å³ in the ammonium ion,¹⁰ the amino-group mean polarisability of 1.75 Å³ was reduced to 1.44 Å³ to allow for the partial positive charge on the nitrogen atoms due to co-ordination. In the computations the mean polarisability of each individual CH_n or NH_n group of the chelate ring was placed in the $[\text{Co}^{\text{III}}\text{N}_6]$ chromophore frame at the position of the corresponding heavy atom, carbon or nitrogen, determined by X-ray crystallography.⁷

The heavy-atom co-ordinates of the *lel* and the *ob* type (S)(+)-propylenediamine chelate ring were taken, respectively, from the crystal structure of the *lel* isomer,¹¹ $\Delta(-)[\text{Co}\{(R)\text{pn}\}_3]\text{Br}_3$, and the *ob* isomer,¹² $\Delta(+)[\text{Co}\{(R)\text{pn}\}_3][\text{Co}(\text{CN})_6]\cdot 2\text{H}_2\text{O}$, the co-ordinates being inverted for reference to the corresponding (S)pn enantiomers. The co-ordinates of the heavy atoms of the chelate ring formed by *N*-methylethylenediamine with the δ conformation were taken, for the *lel* type of atomic displacements, from the crystal structure of ¹³ $\Lambda(+)-[\text{Co}(\text{en})_3]\text{Cl}_3\cdot\text{H}_2\text{O}$, and, for the *ob* type, from that of the *ob* structure,¹⁴ $\Lambda(+)[\text{Co}\{(RR)\text{chxn}\}_3]\text{Cl}_3\cdot\text{H}_2\text{O}$ (chxn = *trans*-cyclohexane-1,2-diamine), the co-ordinates being

inverted in the latter case in order to refer to a chelate ring in the δ conformation. The *N*-methyl group was located on the assumption that it adopts a preferred quasi-equatorial conformation with respect to the mean plane of the chelate ring and that the bonds from the nitrogen atom have a tetrahedral orientation, with a C-N bond length of 1.47 Å.

The results obtained show (Table 1) that the *N*-methyl group substituted into a five-membered diamine chelate ring induces relatively large rotational strengths of opposite sign in two of the components of the ${}^1A_1 \rightarrow {}^1T_1$ transition of octahedral Co^{III} , but that the sum of the contributions of the group over all the three components is small and influences to only a minor degree the magnitude of the total rotational strength of the transition, $R(T_1)$, made up of contributions from all of the groups in the chelate ring to all the three components. The extensive mutual cancellation of the large rotational strengths induced by the *N*-methyl group in components of the ${}^1A_1 \rightarrow {}^1T_1$ transition derives from the location of the group close to a σ_d plane of the octahedron, the cancellation being complete if the group lies in the σ_d plane. The substantial rotational strengths of opposite sign are induced by the *N*-methyl group in the two components of the ${}^1A_1 \rightarrow {}^1T_1$ transition which involve charge displacements in the two σ_h planes sharing a common intersection with the σ_h plane to which the group is proximate, e.g. an intersection along the x axis in the present cases (Figure 4, Table 1). For these two components of the ${}^1A_1 \rightarrow {}^1T_1$ transition the rotational strength due to the *N*-methyl group has a sign opposite to that of the sum of the contributions from all the other groups in the chelated diamine and a larger magnitude, so that *N*-methyl substitution inverts the sign of the rotational strength of those two component excitations (Table 1). So long as the three components of the ${}^1A_1 \rightarrow {}^1T_1$ transition remain degenerate, the sign of the overall, observable, rotational strength, $R(T_1)$, is unaffected by *N*-methyl substitution, owing to the minor effect of the *N*-methyl group summed over the three components (Table 1).

The major contributions to the overall rotational strength, $R(T_1)$, come from the CH and CH₂ groups of the chelate ring. The contributions of a given CH or CH₂ group to the rotational strengths of the individual components of the ${}^1A_1 \rightarrow {}^1T_1$ transition are of opposite sign and partly cancel when summed. However, the sum for such a group is dominated by its contribution to the particular component which involves a charge displacement in the octahedral σ_h plane proximate to the mean plane of the chelate ring, i.e. the $d_{xy} \rightarrow d_{x^2-y^2}$ excitation for a chelate ring spanning the X and the Y axes (Figure 4, Table 1). The dominance arises from the finite extension of the hexadecapolar transition-charge distribution, which makes the potential between the

¹⁰ R. J. W. Le Fevre, *Adv. Phys. Org. Chem.*, 1965, **3**, 1.

¹¹ H. Iwasaki and Y. Saito, *Bull. Chem. Soc. Japan*, 1966, **39**, 92.

¹² R. Juroda and Y. Saito, *Acta Cryst.*, 1974, **B30**, 2126.

¹³ M. Iwata, K. Nakatsu, and Y. Saito, *Acta Cryst.*, 1969, **B25**, 2562.

¹⁴ A. Kobayashi, F. Marumo, and Y. Saito, *Acta Cryst.*, 1972, **B28**, 2709.

dipole of the ligand group L and the nearest pole of the charge distribution q_{oa}^i the major term of the sum S_z^L [equation (4)] and the sign-determining factor in the expression for the rotational strength [equation (5)].

The C -methyl group of the (S)(+)-propylenediamine chelate ring makes little contribution to the rotational strength of any of the components of the ${}^1A_1 \rightarrow {}^1T_1$ transition (Table 1), owing to the proximity of the carbon atom of the group to the adjacent σ_h plane and to the larger distance of the carbon atom from the metal ion (4.2 Å). The substitution of C -alkyl groups or the annelation of a five-membered diamine chelate ring has only a minor effect on the d -electron optical activity of complexes of the type $[\text{Co}(\text{NH}_3)_4(\text{diamine})]^{3+}$ or *trans*- $[\text{Co}(\text{NH}_3)_2(\text{diamine})_2]^{3+}$, the visible c.d. spectra of (4) and (7) (Figure 1) closely resembling those of the corresponding *trans*-(S,S)cyclohexane-1,2-diamine analogues.¹⁵

The overall first-order rotational strength, $R(T_1)$, calculated for the N -methyl- and the C -methyl-substituted ethylenediamine chelate ring with the δ conformation and the *ob* type of group displacements (Figure 3) from the adjacent σ_h plane have the same sign and magnitude, -0.23 in 10^{-40} c.g.s. units (Table 1). In the same units the observed value of $R(T_1)$ per chelate ring for the complexes (4)–(9) agrees in sign and order of magnitude, but is larger, -0.6 .

For a diamine chelate ring in which the group displacements from the proximate σ_h plane are of the *lel* type (Figure 3) the calculated effect of N -alkyl substitution is larger and negative for the σ conformation of the ring (Table 1). The expected effect is observed in the c.d. spectra over the 400–550 nm region of the octahedral 1T_1 absorption of the N -alkyl-substituted complexes (10)–(12) (Figure 2) where the positive c.d. band is smaller in area and the negative c.d. band larger relative to the corresponding c.d. bands of the parent complex, $\Lambda(+)[\text{Co}(\text{en})_3]^{3+}$.

The monochelate and *trans*-bis(diamine) complexes (4)–(9) exhibit only conformational optical activity, due to a chiral puckering of the chelate rings, whereas the *cis*-bis(diamine) and tris(diamine) complexes possess additionally a configurational rotational strength arising from the screw dissymmetry of the mean planes of the chelate rings. The configurational optical activity emerges in the ligand-polarisation model on reducing the symmetry of the $[\text{Co}^{\text{III}}\text{N}_6]$ chromophore from O to D_3 . In a tris(diamine) complex of Co^{III} the three components of the 1T_1 excited octahedral state are no longer necessarily degenerate and linear combinations transforming as 1A_2 and 1E in D_3 are formed, as in (6) where the

$$\psi({}^1A_2, {}^1E) = C_x \chi_{xy}^{x^2-y^2} + C_\beta \chi_{yz}^{y^2-z^2} + C_\gamma \chi_{zx}^{z^2-x^2} \quad (6)$$

coefficients, C_i , assume the values of, e.g., $1/3^{\frac{1}{2}}$ for the 1A_2 state, and the appropriate group-theoretical values ensuring orthonormality for each of the two components of the 1E state.

The transient electric dipoles induced in the ligand groups and correlated coulombically by the hexadecapole moment of each of the original ${}^1A_1 \rightarrow {}^1T_1$ components now

forms a non-zero scalar product with the resulting magnetic dipole moment of all the three components, weighted by the appropriate coefficients, C_i , of equation (6). For a quantitative treatment of the tris(diamine) complexes the octahedral co-ordinate frame (Figure 4) is transformed to a trigonal frame in which the ${}^1A_1 \rightarrow {}^1A_2$ component has a magnetic-dipole moment directed along the z axis, the C_3 axis of the complex, and each of the ${}^1A_1 \rightarrow {}^1E$ components has a magnetic moment of the same magnitude ($2^{\frac{1}{2}}$ Bohr magneton) directed along the x and y axis, respectively. In the trigonal frame the first-order configurational rotational strength of the ${}^1A_1 \rightarrow {}^1A_2$ transition in a D_3 complex is given by the ligand-polarisation treatment as (7) where the sum, $S_{i,z}^L$, refers

$$R(A_2) = im_{\text{ao}}^z \sum_L \bar{\alpha}(L) \sum_{i=\alpha,\beta,\gamma} C_i S_{i,z}^L \quad (7)$$

to the potential of equation (4) between the z component of the point dipole in the ligand group L and the extended $2^{\frac{1}{2}}$ -pole moment of each configurational excitation weighted by the appropriate coefficient C_i in equation (6). The rotational strengths of the two components of the ${}^1A_1 \rightarrow {}^1E$ transition are given by expressions analogous to equation (7) referring to x and to y magnetic-dipole polarisation.

The rotational strength of the latter two components, $R(E)$, for $\Lambda(+)[\text{Co}(\text{en})_3]^{3+}$ has the value of $+53$ in 10^{-40} c.g.s. units from measurements of the axial c.d. spectrum of single crystals containing the complex ion, compared with the value of $+42$ in the same units calculated⁶ from equation (7) and its analogues, employing atomic co-ordinates obtained by a crystal-structure analysis¹³ and the parameters used to estimate the ring-conformation rotational strengths. However, the calculated first-order value of $R(A_2)$ for $\Lambda(+)[\text{Co}(\text{en})_3]^{3+}$ is almost equal in magnitude and opposite in sign, having the ring-conformation optical activity as the main first-order contribution to the net rotational strength, $R(T_1)$, which is measured by the c.d. spectrum of the complex ion randomly oriented in solution.⁶

A non-vanishing contribution from the configurational optical activity, due to the screw disposition of the mean planes of the chelate rings, to the net rotational strength, $R(T_1)$, is afforded by the ligand-polarisation treatment carried to second order.⁶ In the second-order development, the transient dipoles of the ligand groups, themselves correlated by the hexadecapole moment of a component of the ${}^1A_1 \rightarrow {}^1T_1$ d -electron transition in the visible region, coulombically correlate in turn the corresponding component of the electric-dipole moment of the allowed charge-transfer ${}^1A_1 \rightarrow {}^1T_1$ transition exhibited by complexes containing the $[\text{Co}^{\text{III}}\text{N}_6]$ chromophore in the u.v. region. The vacuum u.v. c.d. spectrum of $\Lambda(+)-[\text{Co}(\text{en})_3]^{3+}$ shows two major c.d. bands of opposite sign and approximately equal area in the charge-transfer region.⁶ The lower-frequency negative c.d. band with an extremum at $48\,000\text{ cm}^{-1}$ arises from the D_3 component ${}^1A_1 \rightarrow {}^1E$ of the octahedral charge-transfer transition,

¹⁵ R. S. Treptow, *Inorg. Chem.*, 1966, 5, 1593.

as is shown by the axial single-crystal c.d. spectrum¹⁶ of $2[\Lambda(+)\text{Co}(\text{en})_3\text{Cl}_3]\cdot\text{NaCl}\cdot 6\text{H}_2\text{O}$, and the positive c.d. band at $58\,000\text{ cm}^{-1}$ is due to the corresponding ${}^1A_1 \rightarrow {}^1A_2$ charge-transfer component.

The D_3 components of the ${}^1A_1 \rightarrow {}^1T_1$ d -electron transition of $[\text{Co}(\text{en})_3]^{3+}$ in the visible region are virtually degenerate,¹⁷ so that the energy interval between the A_2 components of the d -electron and the charge-transfer transition is larger than that between the corresponding E components. Accordingly the transfer of an electric-dipole moment from the charge-transfer to the d -electron transition by the second-order ligand-polarisation mechanism is favoured for the E over the A_2 components. Explicitly the z component of the second-order rotational strength has the form (8),⁶ where μ_{ob}^z

$$R_{\delta\alpha}^{(2)}(z) = im_{\alpha 0}^z |\mu_{ob}^z|^2 \rho (E_b - E_a)^{-1} \sum_L \bar{\alpha}(L) [3X_L Z_L S_L^L + 3Y_L Z_L S_L^L + (3Z_L^2 - R_L^2) S_L^L] R_T^{-5} \quad (8)$$

is the z component of the electric-dipole moment and E_b the energy of the charge-transfer transition, while $m_{\alpha 0}^z$ is the corresponding magnetic moment and E_a the energy of the d -electron transition, ρ being an energy ratio of the order of unity. The corresponding expressions for the x and the y components of the second-order rotational strength are obtained from equation (8) by a cyclic permutation of the co-ordinates.

The energy denominator $(E_b - E_a)$ is larger for the A_2 than for the E component of the ${}^1A_1 \rightarrow {}^1T_1$ d -electron transition, while the other terms of equation (8) are of equal magnitude for these components, so that $R^{(2)}(E) > R^{(2)}(A_2)$. The configurational contribution to the net rotational strength, $R(T_1)$, given by the sum of $R(E)$ and $R(A_2)$ taken over the first and second order, is thus non-vanishing and it takes the sign of the major of these two strengths, $R(E)$, namely positive for the Λ configuration of a $[\text{Co}(\text{diamine})_3]^{3+}$ complex containing five-membered

TABLE 2

Calculated and observed rotational strengths R (10^{-40} c.g.s. units) associated with the ${}^1A_1 \rightarrow {}^1T_1$ octahedral transition in D_3 tris(diamine)cobalt(III) complexes. The first- and second-order contributions to the calculated conformational and configurational rotational strengths are combined in the values listed

Complex and structure	$R(A_2)$	$R(E)$	$R(T_1)$	
			calc.	obs.
$\Lambda(+)[\text{Co}\{(S)\text{pn}\}_3\delta\delta\delta]^{3+}$	-61.3	+65.1	+3.76	+4.2
$\Lambda(+)[\text{Co}\{(R)\text{pn}\}_3\lambda\lambda\lambda]^{3+}$	-57.5	+63.3	+5.86	+8.0
$\Lambda(+)[\text{Co}(\text{en})_3\delta\delta\delta]^{3+}$	-59.9	+63.9	+3.97	+4.4
$(+)[\text{Co}(\text{Me-en})(\text{en})_2]^{3+}$	-60.2	+64.1	+3.85	+4.2
$(+)[\text{Co}(\text{Me}_2\text{-en})(\text{en})_2]^{3+}$	-60.6	+64.3	+3.72	+4.0
$(+)[\text{Co}(\text{Pr}^1\text{-en})(\text{en})_2]^{3+}$	-59.1	+63.0	+3.86	+2.8

chelate rings. Values of $R(A_2)$ and $R(E)$ calculated from equations (7) and (8) for the N -alkyl derivatives (10)—(12) of $\Lambda(+)[\text{Co}(\text{en})_3]^{3+}$ and for related complexes are recorded in Table 2, together with the calculated and

observed values of the net rotational strength, $R(T_1)$. The calculations were based on atomic co-ordinates obtained by X -ray crystal-structure analyses¹¹⁻¹³ with the N -alkyl group or groups of (10)—(12) and added to the structure¹³ of $\Lambda(+)[\text{Co}(\text{en})_3]^{3+}$ as described above for the computation of the ring-conformation rotational strengths, and with the group polarisabilities and hexadecapole radius employed in those computations. The first-order ring-conformation rotational strengths of equation (5) were augmented to second order through equation (8) and they are partitioned for the tris(diamine) complexes between $R(A_2)$ and $R(E)$ according to the prescription of equation (6).

The rotational strength $R(E)$ is observable from the axial c.d. spectrum of a uniaxial single crystal containing the complex ion, and theoretical values of $R(E)$ are in satisfactory agreement with the corresponding experimental values, where the latter are available.⁶ More generally, the observable quantity for the randomly oriented complex ion is the net rotational strength, $R(T_1)$, representing the sum of $R(E)$ and $R(A_2)$. In a tris(diamine) complex containing chirally puckered chelate both the ring conformation and the configurational optical activity contribute to $R(T_1)$. The two contributions have the same sign for an *ob* isomer, both being positive for a $\Lambda\lambda\lambda\lambda$ form, whereas the signs are opposed for a *lel* isomer and in a $\Lambda\delta\delta\delta$ form the positive Λ -configurational effect, which is dominant in $\Lambda(+)[\text{Co}(\text{en})_3]^{3+}$ and the C -methyl and N -alkyl derivatives studied, is partly offset by the negative δ -conformation contribution of each chelate ring. Thus both experimentally and theoretically $R(T_1)$ has a larger magnitude for the *ob* form $\Lambda(+)[\text{Co}\{(R)\text{pn}\}_3\lambda\lambda\lambda]^{3+}$ than for the *lel* isomer, $\Lambda(+)[\text{Co}\{(S)\text{pn}\}_3\delta\delta\delta]^{3+}$ (Table 2).

The substitution of an N -methyl group into an ethylenediamine chelate ring appreciably enhances the ring-conformation optical activity if the displacements of the chelate-ring groups from the adjacent σ_h plane are of the *lel* type (Figure 3), whereas a smaller opposite effect results if the displacements are of the *ob* type (Table 1). The n.m.r. evidence indicates¹⁸ that, while *lel* forms predominate, the most abundant conformer of $\Lambda(+)-[\text{Co}(\text{en})_3]^{3+}$ in aqueous solution at ambient temperature is $\delta\delta\lambda$. For the $\Lambda\delta\delta\lambda$ form, the λ ring is of the *ob* type and the δ rings are of the *lel* type, so that N -methyl substitution in either type of chelate ring is expected to give a negative contribution to the ring-conformation optical activity, and thence to $R(T_1)$ in (10) and (11). Both the calculated and the observed values of $R(T_1)$ of (10) and (11) are smaller than the corresponding value for $\Lambda(+)[\text{Co}(\text{en})_3]^{3+}$, and the reduction is proportional to the number of N -methyl groups substituted (Table 2).

The effect of N -alkyl substitution on the d -electron optical activity of $\Lambda(+)[\text{Co}(\text{en})_3]^{3+}$ is similar to that of polarisable oxo-anions^{19,20} such as $[\text{PO}_4]^{3-}$ or $[\text{SeO}_3]^{2-}$

¹⁶ S. F. Mason and A. J. McCaffery, *Mol. Phys.*, 1963, **6**, 359.

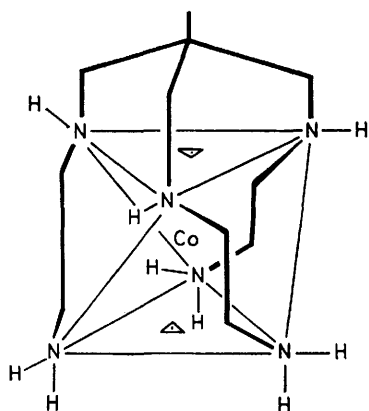
¹⁷ R. Dingle and C. J. Ballhausen, *Mat. fys. Medd.*, 1967, **35**, no. 12.

¹⁸ J. K. Beattie, *Accounts Chem. Res.*, 1971, **4**, 253.

¹⁹ H. L. Smith and B. E. Douglas, *J. Amer. Chem. Soc.*, 1964, **86**, 3885.

²⁰ S. F. Mason and B. J. Norman, *Proc. Chem. Soc.*, 1964, 339; *J. Chem. Soc. (A)*, 1966, 301.

which also change $R(T_1)$ to a more negative value. The X-ray diffraction analysis²¹ of the crystal $[\text{Co}(\text{en})_3]_2 \cdot [\text{HPO}_4]_3 \cdot 9\text{H}_2\text{O}$ supports the structure proposed from the



(13)

c.d. evidence for the $[\text{Co}(\text{en})_3]^{3+}$ ion pair with $[\text{PO}_4]^{3-}$ in which the C_3 axes of the two ions are coincident, with three oxygen atoms of the anion hydrogen-bonded to

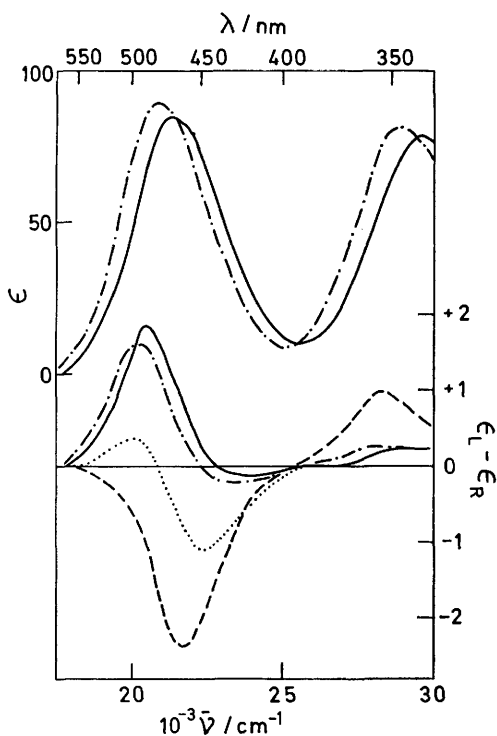


FIGURE 5 Absorption spectra (upper curves) and c.d. spectra (lower curves) of (—) $\Lambda(+)[\text{Co}(\text{en})_3]^{3+}$, (-·-·-) the NN' -dimethyl derivative (11), (····) the capped derivative $\Lambda(+)[\text{Co}(\text{tae})]^{3+}$ (13) (adapted from ref. 22), and (- - -) the bicapped derivative, $\Lambda[\text{Co}(\text{obae})]^{3+}$ (14)

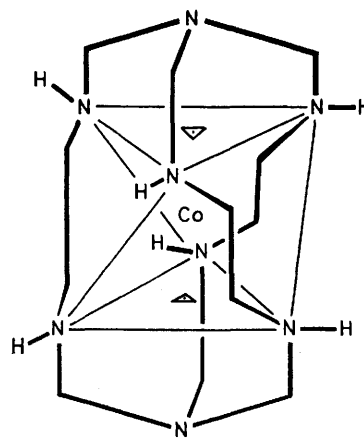
three nitrogen atoms forming a triangular face of the co-ordination octahedron of the cation normal to the C_3 axis.²⁰ That is, a hydrogen-bonded oxygen atom of

²¹ E. N. Duesler and K. N. Raymond, *Inorg. Chem.*, 1971, **10**, 1486.

²² J. E. Sarneski and F. L. Urbach, *J. Amer. Chem. Soc.*, 1971, **93**, 884.

$[\text{PO}_4]^{3-}$ in the ion pair is similarly disposed to the carbon atom of the N -methyl group in $[\text{Co}(\text{Me-en})(\text{en})_2]^{3+}$ (10). The hexadentate ligand, 1,1,1-tris(2'-aminoethylamino-methyl)ethane (tae), forms the complex $\Lambda(+)[\text{Co}(\text{tae})]^{3+}$ (13), designed²² to serve as a model for the $\Lambda(+)[\text{Co}(\text{en})_3]^{3+}$ ion pair with $[\text{PO}_4]^{3-}$. The alkyl groups of the trigonal cap to the ligand in $\Lambda(+)[\text{Co}(\text{tae})]^{3+}$ (13), the groups additional to those present in $\Lambda(+)[\text{Co}(\text{en})_3]^{3+}$, make a large negative contribution to $R(T_1)$, which is now negative overall²² (Figure 5).

The negative contribution is even larger in the recently discovered²³ trigonally bicapped complex, $\Lambda[\text{Co}(\text{oabe})]^{3+}$ (14), containing the ligand, 1,3,6,8,10,13,16,19-octa-azabicyclo[6.6.6]eicosane (Figure 5). The CH_2 groups exocyclic to the ethylenediamine chelate rings of (13) and (14) have a disposition analogous to that of the N -methyl



(14)

group or groups in (10) and (11), although models indicate that the carbon atom of these CH_2 groups is located at a greater distance from the proximate σ_d nodal plane than the N -methyl carbon atom of the latter complexes. The calculated contribution to $R(T_1)$ of a N -methyl or N -methylene group substituted into a five-membered diamine chelate ring of a $[\text{Co}^{\text{III}}\text{N}_6]$ complex is sensitive to the precise location of the carbon atom near the proximate σ_d nodal plane, and its overall contribution changes sign, for example, when the displacements of the chelate-ring groups, for a given conformation, are changed from the *ob* to the *lel* type (Table 1). Thus the exocyclic CH_2 groups forming the cap or caps to the common $\Lambda(+)[\text{Co}(\text{en})_3]^{3+}$ structure in the complexes (13) and (14) make a larger negative contribution to $R(T_1)$, per group, than the N -methyl group or groups in the complexes (10) and (11) (Figures 2 and 5).

EXPERIMENTAL

Preparations.—The N -alkyl derivatives of $[\text{Co}(\text{en})_3]\text{Cl}_3$ were obtained by the addition with stirring of N -methyl-ethylenediamine (Me-en), NN' -dimethylethylenediamine (Me₂-en), or N -isopropylethylenediamine (Prⁱ-en), (0.06

²³ I. I. Creaser, J. MacB. Harrowfield, A. J. Herlt, R. Geue, A. M. Sargeson, M. R. Snow, and J. Springborg, *J. Amer. Chem. Soc.*, in the press.

mol) to a solution of *cis*- or *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride²⁴ (14.2 g, 0.05 mol) in dimethyl sulphoxide (100 cm³) at 60 °C. After 3 h at 60 °C, during which the colour changed to orange-red, the cooled reaction mixture was poured with stirring into acetone (400 cm³). The precipitated complex, after washing with ethanol and reprecipitation from aqueous solution with ethanol, was converted into the perchlorate salt which was recrystallised from water as orange-red needles {[Co(Me-en)(en)₂][ClO₄]₃·H₂O}. Found (Calc.): C, 14.65 (14.8); H, 4.80 (4.95); N, 14.95 (14.8). [Co(Me₂-en)(en)₂][ClO₄]₃. Found (Calc.): C, 17.0 (17.05); H, 4.90 (4.95); N, 15.05 (14.9). [Co(Prⁱ-en)(en)₂][ClO₄]₃. Found (Calc.): C, 18.45 (18.7); H, 5.10 (5.20); N, 14.6 (14.55)%.

Resolutions.—These were achieved with (+)-nitrocamphorate or with (−)[Co(C₂O₄)₃]^{3−}, separable diastereoisomers being unobtainable with (+)-tartrate, antimony (+)-tartrate, dibenzoyl (+)-tartrate, (+)-α-bromocamphorsulphonate, or (−)-tris(catecholato)arsenate(v). The less-soluble diastereoisomer, formed by (+)-nitrocamphorate with (+)[Co(Me-en)(en)₂]³⁺ or with (+)[Co(Me₂-en)(en)₂]³⁺, was recrystallised from water until the c.d. spectrum of the mother liquor and of a solution of the crystals were identical,

when the complex was taken to be optically pure and was converted into its perchlorate salt. The c.d. maxima in aqueous solution are: (+)[Co(Me-en)(en)₂][ClO₄]₃·H₂O, Δε₄₉₀ +1.82; (+)[Co(Me₂-en)(en)₂][ClO₄]₃, Δε₄₉₂ +1.76. The less-soluble diastereoisomer (+)[Co(Prⁱ-en)(en)₂](−)[Co(C₂O₄)₃], after washing with water, was ground with a slurry of potassium iodide and water.²⁵ The solid remaining, (+)[Co(Prⁱ-en)(en)₂]₃I₃, was washed and converted into the corresponding perchlorate salt, which was recrystallised from water until the same c.d. maximum, Δε₅₀₂ +1.38, was attained for the mother liquor and for a solution of the crystals.

Spectra.—These were recorded for aqueous solutions of the perchlorate salts of the *N*-alkyl complexes using Cary 17 (absorption) and Jouan CD185 dichrograph (circular dichroism) spectrometers.

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²⁴ J. C. Bailar, *Inorg. Synth.*, 1946, **2**, 222.

²⁵ J. W. Vaughn, V. E. Magnuson, and G. J. Seiler, *Inorg. Chem.*, 1969, **8**, 1201.