936. *Optical Rotatory Power of Co-ordination Compounds. Part IV.* Spectroscopic and Configurational Assignments for Bisdiamine Complexes*

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Circular dichroism spectra are reported for bisdiamine d^3 and d^6 metal complexes with C_2 symmetry. The optical activity associated with the two $d \longrightarrow d$ absorption bands of *cis*-$Co(en)_2L_2^{3+}$ is found to consist generally of four circular dichroism bands. If the ligand L is unidentate, two circular dichroism bands are observed in the wavelength region of each unpolarised absorption band, but if the ligand LL is bidentate and conjugated one and three circular dichroism bands are associated, respectively, with the longer- and the shorter-wavelength unpolarised absorption.

The results are analysed in terms of a model in which the complexes *cis*-$Co(en)_2L_2^{3+}$ are regarded as intermediate cases between $Co(en)_3^{3+}$ with D_3 symmetry and *cis*-$Co(NH_3)_4L_2^{3+}$ with C_{2v} symmetry. The model provides two independent criteria for the identification of the electronic origin of the circular dichroism given by the complexes *cis*-$Co(en)_2L_2^{3+}$, one based on the relative magnitudes of the bands and the other on the energy-displacement of the bands from a standard frequency provided by the parent trigonal complex $Co(en)_3^{3+}$. The effect of polarisable anions on the circular dichroism band areas affords a third criterion of less-general application. The absolute configurations of the *cis*-series of bisdiamine complexes are derived from the signs of the circular dichroism bands with a known electronic origin.

In the present work, previous studies [1,2] of the relationship of the absolute configuration to the optical activity of dissymmetric co-ordination compounds are extended to the *cis*-series of the bisdiamine complexes of cobalt(III). The electronic absorption and circular dichroism spectra of the complexes investigated are recorded in Table 1 and Figures 1—8.

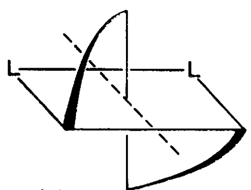
* Part III, A. J. McCaffery, S. F. Mason, and (in part) R. E. Ballard, *J.*, 1965, 2883.

[1] A. J. McCaffery and S. F. Mason, *Mol. Phys.*, 1963, **6**, 359.

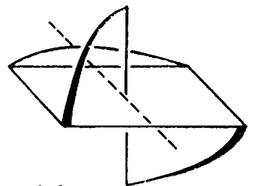
[2] R. E. Ballard, A. J. McCaffery, and S. F. Mason, *Proc. Chem. Soc.*, 1962, 331; *J.*, 1965, 2883.

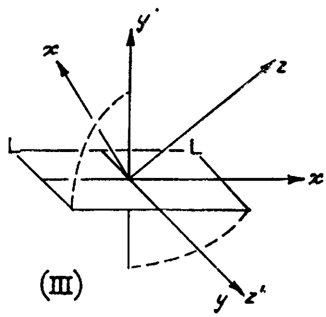
As yet the absolute configuration of no bis-chelate complex of the *cis*-series has been established by *X*-ray diffraction,[3] and the assignment of configuration by the procedures of conformational analysis [4] is less certain in the bis- than in the tris-diamine series owing to the smaller energy differences involved. Equilibration studies of (—)-propylenediamine complexes * show that (+)-Co(—pn)$_2$(ox)$^+$ is more stable [5] than (—)-Co(—pn)$_2$(ox)$^+$ only by 0·20 kcal. in aqueous solution at 25°, whereas (—)-Co(—pn)$_3$$^{3+}$ is more stable [6] than (+)-Co(—pn)$_3$$^{3+}$ by 1·8 kcal. under the same conditions. The latter energy difference was predicted by Corey and Bailar,[4] who showed that (—)-Co(—pn)$_3$$^{3+}$ had the same absolute configuration as (—)-Co(en)$_3$$^{3+}$, the assignment being confirmed by a subsequent *X*-ray diffraction study.[7] However, the former energy difference, which suggests that (+)-Co(—pn)$_2$(ox)$^+$ also has the same configuration as (—)-Co(en)$_3$$^{3+}$, is too small to be reliable, and the circular dichroism evidence (see below) indicates that the configuration of this complex is related, on the contrary, to that of (+)-Co(en)$_3$$^{3+}$.

The bisdiamine complexes (I) studied (Table 1) belong to the point group C_2, and they are related to the corresponding trisdiamine complexes (II) by a common two-fold rotation axis (C_2), which is z' or y in the co-ordinate frame (III). A bisdiamine and the corresponding trisdiamine have a similar stereochemical configuration if the handedness of the chelate rings around the metal ion is the same when viewed along the common two-fold axis. The stereochemical arrangement of the chelate rings about the metal ion [3] in (+)-Co(en)$_3$$^{3+}$ is left-handed or *M* (minus) [8] when viewed along the principal three-fold axis (C_3), but it is right-handed or *P* (positive) [8] when viewed (II) along any of the three two-fold axes (C_2). Thus, the absolute configuration of (+)-Co(en)$_3$$^{3+}$ is specified as either $M(C_3)$ or $P(C_2)$ and that of a bisdiamine complex in the *cis*-series with the same configuration (I) is designated $P(C_2)$.



(I)


(II)



(III)

In a number of current theories [9-11] the optical activity exhibited by the visible absorption bands of dissymmetric metal complexes is ascribed solely to the distortion of the ligand atoms,[9] or their orbitals,[10] or their charges [9,11] from the octahedral disposition. The chelate atoms not directly bonded to the central metal ion, such as the carbon and hydrogen atoms of the diamine complexes, are considered to be electronically inert and serve only to produce mechanically the required distortions. According to such theories

* Ligands are designated by the abbreviations given in the notes appended to Table 1.

[3] K. Nakatsu, M. Shiro, Y. Saito, and H. Kuroya, *Bull. Chem. Soc., Japan*, 1957, **30**, 158.
[4] E. J. Corey and J. C. Bailar, *J. Amer. Chem. Soc.*, 1959, **81**, 2620.
[5] F. P. Dwyer, T. E. MacDermott, and A. M. Sargeson, *J. Amer. Chem. Soc.*, 1963, **85**, 661.
[6] F. P. Dwyer, F. L. Garvan, and L. Shulman, *J. Amer. Chem. Soc.*, 1959, **81**, 290; A. M. Sargeson, " Chelating Agents and Metal Chelates," ed. F. P. Dwyer and D. P. Mellor, Academic Press, London, 1964, p. 183.
[7] Y. Saito, H. Iwasaki, and H. Ota, *Bull. Chem. Soc. Japan*, 1963, **36**, 1543.
[8] R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem.*, 1965, to be published.
[9] T. S. Piper and A. Karipides, *Mol. Phys.*, 1962, **5**, 475; A. G. Karipides and T. S. Piper, *J. Chem. Phys.*, 1964, **40**, 674.
[10] A. D. Liehr, *J. Phys. Chem.*, 1964, **68**, 665.
[11] M. Shinada, *J. Phys. Soc. Japan*, 1964, **19**, 1607.

there is no necessary connection between the stereochemical configuration of a metal complex and the sign of the Cotton effect of a particular electronic transition. These theories require, for example, that two trigonal complexes with the same absolute stereochemical configuration, produced, respectively, by compressing and by elongating the corresponding octahedral complex in the direction of a three-fold axis, would have rotational strengths associated with a given transition of opposite sign.

However, the results of the three [3,12,13] *X*-ray diffraction studies of $Co(en)_3^{3+}$ show that the displacement of the nitrogen atoms from the octahedral positions is very small, and uncertain in direction. Moreover, deuteration studies indicate [14] that the wave functions of the electronic states connected by the transitions which give rise to the several absorption bands of (+)-$Co(en)_3^{3+}$ extend to the N–H bonds, and the sign of the charge-transfer circular dichroism band given by trisdiaminecobalt(III) complexes in the 2200 Å region has been found [15] to depend upon the right- (k') or left-handed (k) conformation [4] of the N–C–C–N chain.

Further, the distortion theories [9-11] require that the ligand-field parameter Dq, measured by the energy of the long-wavelength absorption band, should be smaller in the chelated diamine complexes than in the corresponding hexa-ammine, since the displacement of the nitrogen atom or of its orbitals from the octahedral position reduces the overlap between the e_g d-orbitals of the metal ion and the nitrogen lone-pair σ-orbital, and gives a non-zero overlap between the latter orbital and the t_{2g} d-orbitals of the metal. Thereby the energies of the e_g and the t_{2g} electrons are lowered and raised, respectively, and the

TABLE 1

The absorption and circular dichroism spectra, in aqueous solution, of *cis*-$Co(en)_2L_2^{3+}$ and related complexes. The lowest-energy $d \longrightarrow d$ transitions of the complexes *cis*-$Co(en)_2L_2^{3+}$ are described, in parentheses, by their dominant parentage in the appropriate limiting case of either the A_2 and E_a transitions of $Co(en)_3^{3+}$ or the A_2, B_1, and B_2 transitions of the corresponding C_{2v} complex

		Absorption		Circular dichroism				
Complex [a]	Isomer	$\lambda_{max.}$ (Å)	$\varepsilon_{max.}$	$\lambda_{max.}$ (Å)	$(\varepsilon_l - \varepsilon_r)_{max.}$	Transition	Confign.	Ref.*
$Co(NH_3)_6^{3+}$	—	4760	60			T_{1g}		1
		3420	44			T_{2g}		
(+)-$Co(en)_3^{3+}$	*b, c*	4690	84	4930	+1·89	E_a	$M(C_3)$ $P(C_2)$	1
				4280	−0·166	A_2		
		3400	74	3510	+0·25	E_b		
cis-(+)-$Co(en)_2(NH_3)_2^{3+}$	*b, d*	4700	73	4920	+0·42	(E_a)	$P(C_2)$	—
				4300	−0·04	(A_2)		
		3410	62	3560	+0·056	(E_b)		
(−)-$Co(en)_2(bipy)^{3+}$	*b*	4560	114	4800	−0·95	$(A_2 + E)_a$	$M(C_2)$	—
		3200	12,550	3100	+6·35			
		3120	15,280					
(−)-$Co(en)_2(phen)^{3+}$ ...	*c*	4650	117	4810	−0·78	$(A_2 + E)_a$	$M(C_2)$	31
		3050	6600	3080	+3·0			
		2750	32,000	2720	+11·4			
cis-(+)-$Co(en)_2(CN)_2^{+}$ ...	*e*	4000	99	4410	+0·303	$(A_2 + B_2)$	$P(C_2)$	—
				3670	+0·173	(B_1)		
		3080	100	3330	+0·098			
				3050	−0·052			
		2130	65,000	2430	+1·87			
				2150	−18·7			
cis-(+)-$Co(en)_2(NO_2)_2^{+}$	*d, e, f*	4400	224	4600	+1·4	$(A_2 + B_2)$	$P(C_2)$	—
				4000	−0·65	(B_1)		
		3250	3800	3360	−2·4			
				2880	+1·5			
		2430	26,500	2320	−43			

[12] K. Nakatsu, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Japan*, 1956, **29**, 428.
[13] K. Nakatsu, *Bull. Chem. Soc. Japan*, 1962, **35**, 832.
[14] S. F. Mason and B. J. Norman, *Chem. Comm.*, 1965, 48.
[15] A. J. McCaffery, S. F. Mason, and B. J. Norman, *Chem. Comm.*, 1965, 49.

TABLE 1 (*Continued*)

Complex [a]	Isomer	Absorption $\lambda_{max.}$ (Å)	Absorption $\varepsilon_{max.}$	Circular dichroism $\lambda_{max.}$ (Å)	Circular dichroism $(\varepsilon_l - \varepsilon_r)_{max.}$	Transition	Confign.	Ref.*
cis-(+)-$Co(en)_2(H_2O)^{3+}$	*d*	4950	83	5600	−0·30	(B_1)		—
				4850	+1·05	$(A_2 + B_2)$	$P(C_2)$	
		3610	66	3780	+0·20			
				3400	+0·15			
		2150	19,000	2610	−1·3			
				2320	+5·8			
(+)-$Co(en)_2(ox)^+$	*d*, *f*	5000	103	5200	+2·6	$(A_2 + B_1 + B_2)$	$P(C_2)$	—
		3600	122	3850	+0·09			
				3630	−0·05			
				3350	+0·21			
		2330	19,000	2200	−20			
(+)-Co(− pn)$_2$(ox)$^+$ ...	*f*	5000	125	5150	+3·1	$(A_2 + B_1 + B_2)$	$P(C_2)$	—
		3600	155	3890	+0·20			
				3610	−0·12			
				3330	+0·23			
		2300	28,000	2290	−5·0			
(−)-Co(− pn)$_2$(ox)$^+$ ...	*g*	5000	125	5200	−2·75	$(A_2 + B_1 + B_2)$	$M(C_2)$	—
		3600	155	3850	−0·06			
				3650	+0·02			
				3380	−0·25			
		2300	28,000	2330	+42			
(+)-$Co(en)_2(acac)^{2+}$......	*f*	5050	159	5100	+2·6	$(A_2 + B_1 + B_2)$	$P(C_2)$	—
		3850	*214*	3800	−1·2			
		3300	4300	3250	−9·5			
		2550	*17,000*	2500	−9·5			
(+)-$Co(en)_2(CO_3)^+$	*d*, *f*, *h*	5130	143	5300	+3·7	$(A_2 + B_1 + B_2)$	$P(C_2)$	—
		3610	131	3900	+0·27			
				3630	−0·10			
				3440	+0·15			
		2290	47,000	2300	−12			
cis-(−)-$Co(en)_2(N_3)_2^+$ ...	*h*	5200	340	5700	−0·65	(B_1)		—
				5030	+1·2	$(A_2 + B_2)$	$P(C_2)$	
		3130	12,000	3950	−1·6			
				3250	−4·0			
				2700	+7·2			
cis-(+)-$Co(en)_2(Cl)_2^+$ ...	*e*, *g*	*6200*	*30*	6150	−0·6	(B_1)		—
		5350	69	5380	+0·7	$(A_2 + B_2)$	$P(C_2)$	
		3880	*75*	4200	+0·2			
		3180	*560*	3000	−1·1			
		2350	16,000	2650	+6·0			
				2400	−15			
cis-(+)-$Cr(en)_2(Cl)_2^+$ ...	*e*	*5900*	*20*	5900	−0·5	(B_1)		—
		5400	74	5200	+0·6	$(A_2 + B_2)$	$P(C_2)$	
		4060	76	4250	+0·25			
				3850	−0·15			
		2150	10,000	2550	−1·0			
(+)-$Cr(en)_2(ox)^+$	*i*	4800	90	4800	+1·9	$(A_2 + B_1 + B_2)$	$P(C_2)$	23*b*

* Present work if not stated otherwise.

(*a*) Ligands are described by the abbreviations: en = ethylenediamine, bipy = 2,2′-bipyridyl, phen = 1,10-phenanthroline, ox = oxalate, −pn = (−)-propylenediamine, acac = acetylacetonate. (*b*) The isomer forming the less-soluble (−)-$Co(ox)_3^{3-}$ salt. (*c*) The isomer forming the less-soluble antimonyl (+)-tartrate salt. (*d*) Prepared from *cis*-(+)-$Co(en)_2(Cl)_2^+$. (*e*) The isomer forming the less-soluble (+)-α-bromocamphorsulphonate salt. (*f*) The isomer forming the less-soluble (+)-$Co(en)(ox)_2^-$ salt. (*g*) The isomer forming the more-soluble (+)-$Co(en)(ox)_2^-$ salt. (*h*) The isomer forming the more-soluble antimonyl (+)-tartrate salt. (*i*) Prepared from *cis*-(+)-$Cr(en)_2(Cl)_2^+$.

energy difference between the two sets (10*Dq*) is reduced. However, the energy of the long-wavelength absorption band (10*Dq*) increases in passing from $Co(NH_3)_6^{3+}$ to the corresponding chelated amine complexes (Table 1).

These observations suggest that in chelated diamine complexes the t_{2g} electrons of the metal ion are partly delocalised into antibonding σ-orbitals spanning the carbon and hydrogen as well as the nitrogen atoms of the diamine chain. The delocalisation lowers the energy of the t_{2g} electrons, thus increasing *Dq*, and it has a cloud-expanding effect which reduces the electron-repulsion parameter B, measured by the energy interval ($16B$) between the longer- and the shorter-wavelength ligand-field absorption band. A decrease in this energy interval results from chelation (Table 1).

In trigonal complexes the triple degeneracy of the t_{2g} orbitals is split into the level t_0 and the doubly degenerate level $t_{\pm}$, with the respective symmetries A_1 and E in the group D_3 (Table 2). The charge density of an electron in the t_0 orbital is concentrated in the

TABLE 2

Trigonal d-orbitals in real form, and their representations in the groups C_2 and D_3. The co-ordinates are as in (III)

Orbital	C_2	D_3	Orbital	C_2	D_3
$t_0 = d_{z^2}$	A	A_1	$e_+ = (1/\sqrt{3})(d_{x^2-y^2} + \sqrt{2}d_{xz})$ ...	A	E
$t_+ = (1/\sqrt{3})(\sqrt{2}d_{x^2-y^2} - d_{xz})$ ...	A	E	$e_- = (1/\sqrt{3})(d_{xy} - \sqrt{2}d_{yz})$	B	
$t_- = (1/\sqrt{3})(\sqrt{2}d_{xy} + d_{yz})$	B				

TABLE 3

The one-electron excited configurations of the cobalt(III) ion constructed from the trigonal d-orbitals (Table 2). A difference in electron spin is denoted by a bar

$$\phi_1 = t_0\bar{t}_0t_+\bar{t}_+t_-\bar{e}_- \qquad \phi_3 = t_0\bar{t}_0t_+\bar{t}_+t_-\bar{e}_+ \qquad \phi_5 = \bar{t}_0t_+\bar{t}_+t_-\bar{t}_-e_+$$
$$\phi_2 = t_0\bar{t}_0t_-\bar{t}_-t_+\bar{e}_+ \qquad \phi_4 = t_0\bar{t}_0t_-\bar{t}_-t_+\bar{e}_- \qquad \phi_6 = \bar{t}_0t_+\bar{t}_+t_-\bar{t}_-e_-$$

direction of the three-fold axis of a trisdiamine complex whereas the electronic charge density of the $t_{\pm}$ orbitals is concentrated towards a plane perpendicular to the C_3 axis in the direction of the carbon and the hydrogen atoms of the chelate rings. The spatial distribution of charge density in the trigonal d-orbitals suggests that the delocalisation of the d-electrons into the antibonding σ-orbitals of the diamine chelate rings preferentially stabilises the $t_{\pm}$ orbitals in accordance with the observation [1,2] that the $t_{\pm}$ level lies below t_0 in the trisdiamine complexes of cobalt(III), chromium(III), and rhodium(III).

The optical activity of chelated diamine complexes arises from the mixing of the $d \longrightarrow d$ transitions of the metal ion with charge-transfer transitions of the ligand σ-electrons to the e_g orbitals of the metal, and of metal t_{2g} electrons to the antibonding σ-orbitals of the ligand in the delocalised d-electron model, which suggests, contrary to the distortion theories,[9-11] that the stereochemical configuration of the chelate rings around the metal ion is related to the sign of the Cotton effect associated with a particular transition.

In a dissymmetric molecule an optically-active transition has both an electric and a magnetic moment, the scalar product of the two moments representing the rotational strength which is measured experimentally by the band area of the corresponding circular dichroism absorption. The long-wavelength absorption band of the octahedral complexes of strong-field d^6 metal ions is due to a transition of T_{1g} symmetry * with a magnetic moment [16] of $\sqrt{24}\beta_M$, where β_M is the Bohr magneton, whilst the higher-energy transition with T_{2g} symmetry, responsible for the shorter-wavelength band, has zero magnetic moment. The magnetic moment is partitioned predominantly between the components deriving from the triply degenerate T_{1g} transition in complexes with symmetry lower than octahedral, and these component excitations, of the several $d \longrightarrow d$ transitions, have the major rotational strengths in the dissymmetric complexes.

The octahedral T_{1g} transition is broken down in the D_3 trigonal complexes (II) such as $Co(en)_3^{3+}$ into a component of A_2 symmetry with an electric and a magnetic moment directed along the three-fold (C_3) axis of the complex, and a doubly degenerate component (E_a) with moments directed perpendicular to the C_3 axis (III). Similarly, the

* The symmetry of a transition denotes the direct product of the irreducible representations of the electronic states connected by the transition. In the case of cobalt(III) the symmetry of a transition from the ground state is identical with the representation of the upper state, as the ground state is totally symmetric.

[16] W. Moffitt, *J. Chem. Phys.*, 1956, **25**, 1189.

octahedral T_{2g} transition is broken down in the dihedral complex (II) into a forbidden component of A_1 symmetry and a doubly degenerate component (E_b) polarised perpendicular to the C_3 axis (III). The circularly polarised crystal spectrum [1] shows that the rotational strengths of the E_a, A_2, and E_b transitions of (+)-$Co(en)_3^{3+}$ are +79, −75, and +2, respectively, in units of 10^{-40} c.g.s. In solution, where the complex ions are randomly orientated, the A_2 and E_a circular dichroism bands overlap and mutually cancel to within 5% owing to the small energy interval (~100 cm.$^{-1}$) between the two transitions, but the circular dichroism due to the components of the octahedral T_{1g} transition remains predominant. The signs of the large, first-order, rotational strengths of the A_2 and the E_a transitions are related [2] to the absolute configuration of the chelate rings round the metal ion in trigonal D_3 complexes (II), but the sign of the weak, second-order rotational strength of the E_b transition is unrelated to that configuration.[15]

These observations suggest the selection of the components of the octahedral T_{1g} transition for the correlation of configuration with optical activity in the *cis*-series of bisdiamine complexes.[17] In the *cis*-complexes with C_2 symmetry (I) the octahedral T_{1g} transition breaks down into one component with A symmetry and two components with B symmetry. The transition with A symmetry derives from the component of the doubly-degenerate E_a transition of the corresponding trigonal complex (II) with an electric and magnetic moment directed along the particular two-fold axis (y) which becomes the principal axis (z') (III) of the *cis*-complex (I), whilst the other E_a component and the A_2 component of the trigonal complex (II) become transitions of B symmetry in the *cis*-complex (I) with moments directed perpendicular to the two-fold axis (z') (III). The three transitions can be distinguished by their symmetry and parentage as $A(E_a)$, $B(E_a)$, and $B(A_2)$.

In general, the transitions $B(E_a)$ and $B(A_2)$ are mixed in the *cis*-complexes, but the upper state of the $A(E_a)$ transition has a wave function which is invariant in form throughout the series $Co(en)_3^{3+}$, *cis*-$Co(en)_2L_2^{3+}$, *cis*-$Co(NH_3)_4L_2^{3+}$, where L is a neutral unidentate ligand or LL is the corresponding bidentate ligand (Tables 2—4). In the general case the ligand L may have a negative charge n when the overall charge of the complex is reduced by $2n$.

The trigonal d-orbitals in real form,[18] t_0, $t_\pm$, and $e_\pm$ (Table 2), provide a basis for the irreducible representations of the groups O_h, D_3, and C_2, but not of the group C_{2v} to which the *cis*-tetra-amine complexes, $Co(NH_3)_4L_2^{3+}$, belong. However, combinations of these orbitals are spanned by the representations of the group C_{2v}, and t_0, $t_\pm$, and $e_\pm$ may be used to construct the excited configurations (Table 3) and excited states (Table 4) of both $Co(en)_3^{3+}$ and a *cis*-tetra-aminecobalt(III) complex. The excited states of the former [9-11,17] and of the latter [19] complex have been described in terms of the complex trigonal d-orbitals and the real tetragonal d-orbitals, respectively.

The results show (Table 4) that the excited state $A(E_a)$ of a C_2 complex $Co(en)_2L_2^{3+}$ has the same orbital construction in the D_3 limit of $Co(en)_3^{3+}$, where the digonal perturbation due to the ligand L vanishes, as in the C_{2v} limit of *cis*-$Co(NH_3)_4L_2^{3+}$, where the chelation or pseudo-trigonal perturbation is zero. However, each of the two B states with T_{1g} octahedral parentage has different forms at the two limits (Table 4), and their wave functions for the intermediate case of the C_2 complex (I) are not symmetry-determined. Thus, the rotational strength of the $A(E_a)$ transition should provide a more reliable basis [17] for the correlation of optical activity with configuration in the series of C_2 complexes (I) than that of the other components of the octahedral T_{1g} manifold, in the cases where this transition can be distinguished.

A sum-rule indicates [9-11,20-22] that the rotational strengths R of the A_2 and the E_a

[17] S. F. Mason, *Quart. Rev.*, 1963, **17**, 20.
[18] C. J. Ballhausen, " Introduction to Ligand Field Theory," McGraw-Hill, London, 1962, p. 68.
[19] H. Yamatera, *Bull. Chem. Soc. Japan*, 1958, **31**, 95.
[20] S. Sugano, *J. Chem. Phys.*, 1960, **33**, 1883.
[21] N. K. Hamer, *Mol. Phys.*, 1962, **5**, 339.
[22] H. Poulet, *J. Chim. phys.*, 1962, 584.

transitions of D_3 cobalt(III) complexes are of opposite sign and have equal or nearly equal magnitudes,

$$R[A_2] + R[E_a] \sim 0 \tag{1}$$

Experimentally, $R[E_a]$ is positive for (+)-$Co(en)_3^{3+}$, and it has a magnitude some 5% larger than $R[A_2]$ which is negative.[1] The rotational strengths of the C_2 complexes *cis*-$Co(en)_2L_2^{3+}$ with excited-state wave functions of the D_3 form have the same sign and probably the same relative magnitude as the corresponding rotational strengths of the $Co(en)_3^{3+}$ isomer with the same absolute configuration. The absolute rotational strengths of the C_2 complexes in which the ligand L is unidentate are probably smaller, owing to the reduced chelation, but the proportionality constant need not be considered explicitly for the present purpose as only the relative theoretical values are compared with experiment.

The rotational strength of the $A(E_a)$ transition of the complexes *cis*-$Co(en)_2L_2^{3+}$, with the same absolute configuration $P(C_2)$ of the chelate rings around the metal ion as (+)-$Co(en)_3^{3+}$, is positive, and in the present approximation it has the value

$$R[A(E_a)] = R[E_a]/2 \tag{2}$$

at either the D_3 limit or the C_{2v} limit, where the transition is re-labelled $A(A_2)$ without change of form (Table 4).

TABLE 4

The wavefunctions ψ of the excited states with T_{1g} and T_{2g} octahedral parentage O_h of the *cis*-complexes $Co(en)_2L_2^{3+}$ in the trigonal limit D_3 and in the non-chelated limit C_{2v}, and the energies E and the magnetic moment polarisation direction P in the co-ordinate frame (III) of transitions to those states from the ground state. K is the trigonal field parameter where $2K$ and $-K$ is the energy displacement of t_0 and $t_{\pm}$, respectively, due to chelation in the parent D_3 complex, and δ, with σ and π components, is the digonal perturbation due to the ligands L which displaces the energy of e_+ and e_- by $\delta/6$ and $\delta/2$ in the corresponding C_{2v} complex *cis*-$Co(NH_3)_4L_2^{3+}$. The function $\psi X(Y)$ has X symmetry in the group C_2 with the parentage of Y symmetry in the group D_3 or C_{2v}

Limit	ψ	P	E	O_h parentage
D_3	$\psi B(A_2) = (1/\sqrt{2})(\phi_3 - \phi_4)$	z	$E_0 - K$	T_{1g}
	$\psi A(E_a) = (1/2)(\sqrt{2}\phi_5 + \phi_1 - \phi_2)$	y	$E_0 + K/2$	
	$\psi B(E_a) = (1/2)(\sqrt{2}\phi_6 + \phi_3 + \phi_4)$	x	$E_0 + K/2$	
	$\psi A(A_1) = (1/\sqrt{2})(\phi_1 + \phi_2)$	—	$E_0' - K$	T_{2g}
	$\psi A(E_b) = (1/2)(\phi_1 - \phi_2 - \sqrt{2}\phi_5)$	—	$E_0' + K/2$	
	$\psi B(E_b) = (1/2)(\phi_3 + \phi_4 - \sqrt{2}\phi_6)$	—	$E_0' + K/2$	
C_{2v}	$\psi B(B_1) = (1/\sqrt{3})(\sqrt{2}\phi_4 + \phi_6)$	y'	$E_0 + \delta\sigma/2 + \delta\pi/2$	T_{1g}
	$\psi A(A_2) = (1/2)(\sqrt{2}\phi_5 + \phi_1 - \phi_2)$	z'	$E_0 + \delta\sigma/4 + \delta\pi/4$	
	$\psi B(B_2) = (1/2\sqrt{3})(3\phi_3 - \phi_4 + \sqrt{2}\phi_6)$	x'	$E_0 + \delta\sigma/4 + \delta\pi/4$	
	$\psi A(A_1) = (1/\sqrt{3})(\sqrt{2}\phi_2 + \phi_5)$	—	$E_0' + \delta\sigma/6 + \delta\pi/2$	T_{2g}
	$\psi A(A_2) = (1/2\sqrt{3})(3\phi_1 + \phi_2 - \sqrt{2}\phi_5)$	—	$E_0' + 5\delta\sigma/12 + \delta\pi/4$	
	$\psi B(B_2) = (1/2)(\phi_3 + \phi_4 - \sqrt{2}\phi_6)$	—	$E_0' + 5\delta\sigma/12 + \delta\pi/4$	

The transitions of B symmetry with octahedral T_{1g} parentage in the C_2 complexes have rotational strengths

$$R[B_a] = c^2R[A_2] + (1/2)(1 - c^2)R[E_a] \tag{3}$$

and

$$R[B_b] = (1 - c^2)R[A_2] + (c^2/2)R[E_a] \tag{4}$$

since the upper states of the two B transitions have the general forms

$$\psi B_a = c\psi B(A_2) - (1 - c^{2\frac{1}{2}})\, \psi B(E_a) \tag{5}$$

and

$$\psi B_b = (1 - c^{2\frac{1}{2}})\, \psi B(A_2) + c\psi B(E_a) \tag{6}$$

where c is a mixing coefficient.

At the D_3 limit the coefficient c is unity and the B_a and B_b transitions become, respectively, the $B(A_2)$ and the $B(E_a)$ components with the rotational strengths $R[A_2]$ and $R[E_a]/2$, respectively. At the C_{2v} limit the coefficient c has the value $(1/\sqrt{3})$ and the B_a and B_b components are the B_1 and the B_2 transitions, respectively (Table 4).

In general the mixing coefficient (eqns. 3—6) has the value $1 > c > 1/\sqrt{3}$ for the C_2 complexes *cis*-$Co(en)_2L_2^{3+}$. Of the various complexes studied (Table 1), *cis*-(+)-$Co(en)_2(NH_3)_2^{3+}$ lies closest to the D_3 limit, $c = 1$. The circular dichroism and unpolarised absorption spectra of this complex and of (+)-$Co(en)_3^{3+}$ are of similar form (Figure 1). In particular, the E_a, A_2, and E_b circular dichroism bands of (+)-$Co(en)_3^{3+}$ have the same relative areas as the corresponding bands of *cis*-(+)-$Co(en)_2(NH_3)_2^{3+}$, suggesting that in the latter complex the splitting of either the E_a or E_b transition into separate A and B components, and the mixing of the components with the same symmetry in the group C_2,

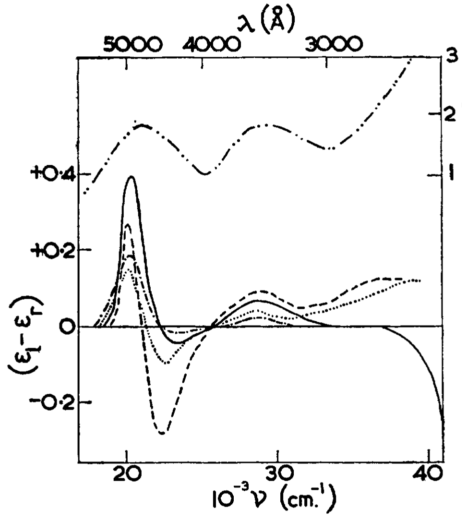


FIGURE 1. The circular dichroism spectrum *cis*-(+)-$Co(en)_2(NH_3)_2(ClO_4)_3$, in water (———) and in 0·2M-aqueous sodium selenite (— — —), and of (+)-$Co(en)_3(ClO_4)_3$ in water (— · — · —) and in 0·2M-aqueous sodium selenite (· · · ·). The absorption spectrum of *cis*-$Co(en)_2(NH_3)_2(ClO_4)_3$ in water (— ·· — ·· —). The left-hand ordinate scale refers directly to the circular dichroism of *cis*-(+)-$Co(en)_2(NH_3)_2^{3+}$ and to the circular dichroism of (+)-$Co(en)_3^{3+}$ divided by ten

is very small. Like (+)-$Co(en)_3^{3+}$, *cis*-(+)-$Co(en)_2(NH_3)_2^{3+}$ gives only one circular dichroism band, due to the E_b transition, in the wavelength region of the octahedral T_{2g} absorption, whereas the other C_2 complexes studied give generally two or three circular dichroism bands in that region, although in some cases, *e.g.*, (+)-$Co(en)_2(acac)^{2+}$, the region is obscured by strong charge-transfer absorption (Table 1; Figures 1—8). Thus, the $A(A_1)$ transition is forbidden in *cis*-(+)-$Co(en)_2(NH_3)_2^{3+}$, like the parent transition in (+)-$Co(en)_3^{3+}$, indicating that the digonal perturbation, due to differences between the ammonia and the ethylenediamine ligand, is small. Since the circular dichroism band arising from the A and B components of the E_a transition is of positive sign (Figure 1), it is concluded that *cis*-(+)-$Co(en)_2(NH_3)_2^{3+}$ has the same $P(C_2)$ configuration (I) as (+)-$Co(en)_3^{3+}$ (II).

The remaining *cis*-$Co(en)_2L_2^{3+}$ complexes give a long-wavelength absorption band displaced by more than 1000 cm.$^{-1}$ from that of $Co(en)_3^{3+}$. Depending upon the position of the ligand L above or below that of amines in the spectrochemical series, the displacement is to higher or to lower frequencies (Table 1). Thus, the digonal perturbation of the ligand L is dominant in the complexes *cis*-$Co(en)_2L_2^{3+}$ if L is not an amine ligand, since the frequency interval [1] between the E_a and the A_2 transitions of $Co(en)_3^{3+}$, due to chelation, is no more than 100 cm.$^{-1}$.

Such complexes give two circular dichroism bands in the region of the long-wavelength absorption band if the ligands L are unidentate but only one circular dichroism absorption if LL is a bidentate ligand (Table 1; Figures 2—8). Whether the unidentate ligand L lies above or below the amines in the spectrochemical series, the major of the two circular

FIGURE 2

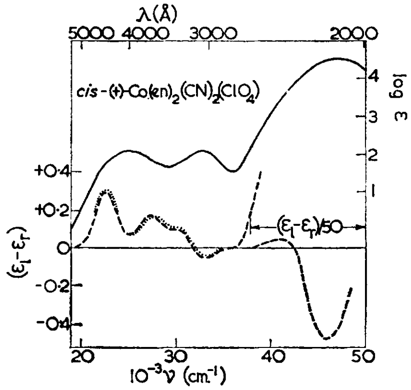


FIGURE 3

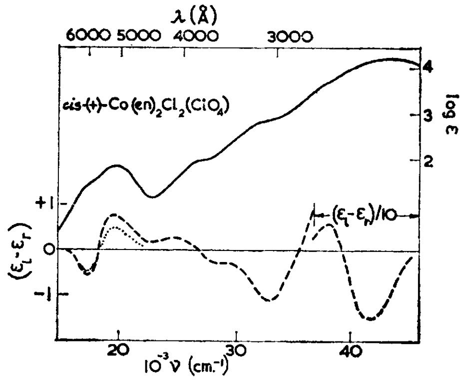


FIGURE 4

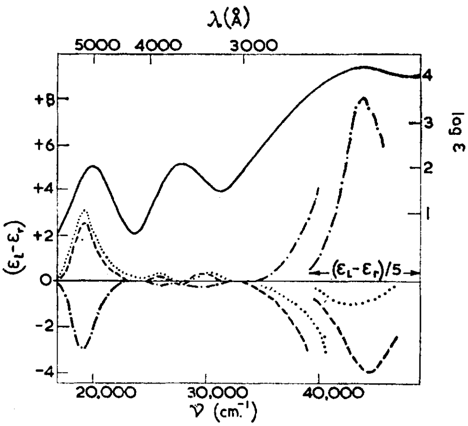


FIGURE 5

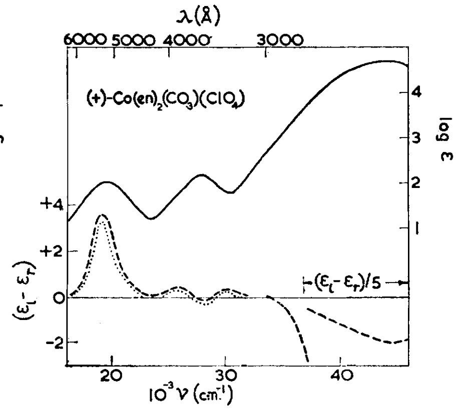


FIGURE 6

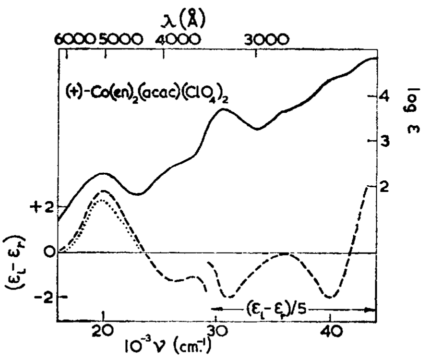


FIGURE 7

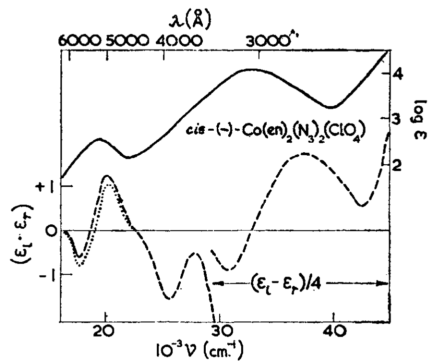
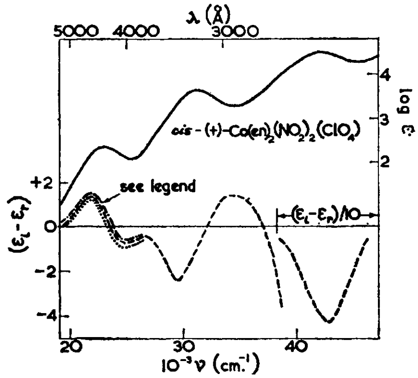


FIGURE 8



FIGURES 2—8. Circular dichroism spectra in water (— — —) and in 0·2M-aqueous sodium selenite (· · · ·), and absorption spectra in water (———)

In Figure 4, curves B and D are the circular dichroism spectra, in water, of (+)-Co(−pn)$_2$(ox)(ClO$_4$) and (−)-Co(−pn)$_2$(ox)-(ClO$_4$), respectively

In Figure 8, the fourth curve is the circular dichroism spectrum in 1·5M-aqueous sodium selenite dichroism bands always lies closer in frequency than the minor to the centre of gravity of the E_a and A_2 circular dichroism bands of (+)-Co(en)$_3^{3+}$ (Table 1). This observation suggests that the minor and the major or long-wavelength circular dichroism bands of *cis*-Co(en)$_2$L$_2^{3+}$, where L is unidentate and not an amine, are due, respectively, to the $B_a(B_1)$ and to the combined $A(A_2)$ and $B_b(B_2)$ components derived from the octahedral T_{1g} transition of cobalt(III).

For *cis*-Co(en)$_2$L$_2^{3+}$ complexes near to the C_{2v} limit the $B_a(B_1)$ component is displaced in energy from the centre of gravity of the A_2 and the E_a transitions of Co(en)$_3^{3+}$ by $\sim\delta/2$, but the $A(A_2)$ and the $B_b(B_2)$ components are each displaced from that centre by $\sim\delta/4$ (Table 4), where δ, covering both the σ and the π perturbations is the difference between the ligand-field parameter $10Dq$ for Co(en)$_3^{3+}$ and CoL$_6^{3+}$. The $A(A_2)$ and $B_b(B_2)$ transitions of *cis*-Co(en)$_2$L$_2^{3+}$ are effectively degenerate, except where LL is a π-bonding chelate ligand, and they give a single circular dichroism absorption with a rotational strength

$$R[A(A_2)] + R[B_b(B_2)] = (1/2)(1 + c^2)R[E_a] + (1 - c^2)R[A_2] \qquad (7)$$

from eqns. (2) and (4). The mixing coefficient has the limiting lower value $c = 1/\sqrt{3}$ for which, from eqn. (3),

$$R[B_a(B_1)] = (1/3)(R[E_a] + R[A_2]) \qquad (8)$$

whilst the $A(A_2)$ and $B_b(B_2)$ transitions have a total rotational strength (eqn. 7) with the same sign and twice the magnitude.

The circular dichroism spectrum of *cis*-(+)-Co(en)$_2$(CN)$_2^+$ (Figure 2) approximates to the limiting case $c \simeq 1/\sqrt{3}$. Both of the circular dichroism bands under the long-wavelength absorption are positive in sign, and the major band, which is displaced less than the minor from the reference absorption frequency of (+)-Co(en)$_3^{3+}$, has an area approximately twice that of the minor band, although the precise area of the latter cannot be estimated as it is partly overlaid by a circular-dichroism band associated with the higher-frequency octahedral T_{2g} absorption (Table 1; Figure 2). Were the sum-rule (eqn. 1) exactly obeyed, each of the rotational strengths of eqn. (8) and eqn. (7) with $c = 1/\sqrt{3}$ would vanish identically, but for the parent trigonal complex,[1] (+)-Co(en)$_3^{3+}$,

$$|R[E_a]| > |R[A_2] \qquad (9)$$

so that a *cis*-Co(en)$_2$L$_2^{3+}$ complex with excited states governed by the lower limiting value of the mixing coefficient $c \sim 1/\sqrt{3}$ gives two low-frequency circular-dichroism bands which both have the same sign as the parent rotational strength $R[E_a]$. As these circular dichroism bands are both positive (Figure 5) it is concluded that *cis*-(+)-Co(en)$_2$(CN)$_2^+$ has the same $P(C_2)$ configuration as (+)-Co(en)$_3^{3+}$.

The lower excited states of the complexes *cis*-Co(en)$_2$L$_2^{3+}$, where the ligand L is unidentate and neither an amine nor cyanide, are determined by values of the mixing coefficient lying towards the smaller limit of the D_3 to C_{2v} range, $1 > c > 1/\sqrt{3}$. The parent rotational strengths, $R[A_2]$ and $R[E_a]$ of Co(en)$_3^{3+}$, then contribute predominantly to $R[B_a(B_1)]$ (eqn. 4) and to $(R[A(A_2)] + R[B_b(B_2)]$ (eqn. 7), respectively, and the sign of the corresponding circular-dichroism band of the C_2 complex reflects the sign of the dominant parent rotational strength for a given absolute configuration. The inequality of eqn. (9) indicates that the minor low-frequency circular-dichroism band of the C_2 complexes is due to the $B_a(B_1)$ component transition and the major to the $A(A_2)$ and $B_b(B_2)$ components.

Thus, the two circular-dichroism bands of the complexes *cis*-Co(en)$_2$L$_2^{3+}$ originating from the components of the octahedral T_{1g} transition may be assigned by means of two independent criteria, namely, relative band area, and displacement from the reference frequency of the Co(en)$_3^{3+}$ absorption. The frequency-displacement criterion is supported by a semi-quantitative relationship between the frequency of the unpolarised absorption and that of each of the two circular-dichroism bands (Figure 9). Whilst the components of the octahedral T_{1g} transition give separate circular-dichroism bands, they are generally unresolved in the unpolarised absorption, a possible exception being the case[23] of *cis*-$Co(en)_2Cl_2{}^+$ where a shoulder is perceptible upon the low-frequency side of the first absorption band (Figure 3). The displacement of the unpolarised absorption from the reference frequency of the $Co(en)_3{}^{3+}$ band is the mean ($\delta/3$) of that of the T_{1g} components (Table 4), so that a plot of the frequency of the long-wavelength absorption band ν_{abs} of the *cis*-$Co(en)_2L_2{}^{3+}$ complexes against the frequency of the major $\nu[A(A_2), B_b(B_2)]$ and the minor $\nu[B_a(B_1)]$ circular dichroism band should give linear relationships with slopes of 3/4 and of 3/2, respectively. The slopes of the observed relationships (Figure 9) are

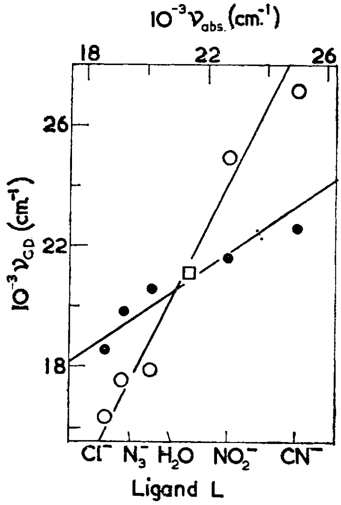


FIGURE 9. The relationships between the frequency of the unpolarised absorption ν_{abs} and the frequency of the major (○) and the minor (●) circular dichroism band $\nu_{C.D.}$ due to the components of the octahedral T_{1g} transition for the complexes *cis*-$Co(en)_2L_2{}^{3+}$. The point □ refers to the mean frequency of the A_2 and the E_a circular dichroism bands and the absorption frequency of the parent trigonal complex $Co(en)_3{}^{3+}$ obtained from the crystal spectra [1]

0·6 and 2·0, respectively, the divergence from the theoretical values being due in part to the overlap of the two circular dichroism bands, which has the general effect of increasing the observed frequency interval between them.

The application of the band-area and the frequency-displacement criteria afford mutually consistent assignments of the origin of the two circular-dichroism bands given by the complexes *cis*-$Co(en)_2L_2{}^{3+}$, where the ligand L is unidentate, in the region of the long-wavelength absorption. For the *cis*-complexes with the same $P(C_2)$ configuration (I) as (+)-$Co(en)_3{}^{3+}$ (II) the major of the two circular dichroism bands, due to the $A(E_a)$ and $B_b(E_a)$ components near to the D_3 limit or to the $A(A_2)$ and $B_b(B_2)$ components near to the C_{2v} limit, has a positive sign, and it is displaced less than the minor band from the reference frequency of the $Co(en)_3{}^{3+}$ absorption. The sign of the minor circular dichroism band is variable, depending upon the value of the mixing coefficient c (eqns. 3—7), and it does not afford a general guide to the configuration of the complex

The dissymmetry of the complexes *cis*-$Co(en)_2L_2{}^{3+}$ derives entirely from the ethylenediamine chelate rings if the ligands L are unidentate, and eqns. (2)—(8), relating the rotational strengths of the *cis*-complexes to those of the parent trigonal complex $Co(en)_3{}^{3+}$, are better approximations for L unidentate than for the cases where LL is a bidentate ligand. The complex $Co(en)_2(ox)^+$, for example, is descended from $Co(en)_3{}^{3+}$, and also, at greater remove, from $Co(ox)_3{}^{3-}$. However, the inequality of eqn. (9) obtains[2] for the trisoxalato- and the tris-(β-dicarbonyl)-complex of cobalt(III), and so it is probable that the single circular dichroism band given by (+)-$Co(en)_2(ox)^+$ and (+)-$Co(en)_2(acac)^{2+}$ in the region of the octahedral T_{1g} absorption (Table 1; Figures 4 and 6) has a sign reflecting that of the dominant rotational strength $R[E_a]$ of the parent trigonal complexes. On this basis, the complexes $Co(en)_2L_2{}^{3+}$, where LL is a bidentate ligand, have the same $P(C_2)$ configuration as (+)-$Co(en)_3{}^{3+}$ if the long-wavelength circular dichroism band is positive in sign.

[23] J. P. Mathieu, *Bull. Soc. chim. France*, 1936, **3**, (*a*) 463, (*b*) 476.

The *cis*-complexes $Co(en)_2L_2^{3+}$, with LL bidentate, give three circular dichroism bands in the shorter-wavelength region of the octahedral T_{2g} absorption (Table 1; Figures 4 and 5). Yamatera has shown [19] for the C_{2v} complexes *cis*-$Co(NH_3)_4L_2^{3+}$ that, if the energy splittings due to the π and the σ perturbations of the ligands L are additive for the components of the octahedral T_{1g} transition, they are subtractive for the components of the octahedral T_{2g} transition, and *vice versa* (Table 4). However, the A_2 and B_2 components of neither the T_{1g} nor the T_{2g} cobalt(III) state are resolved [19] if the ligand L is unidentate, and the *cis*-complexes $Co(en)_2L_2^{3+}$ with L unidentate are found to give only two circular dichroism bands under either the T_{1g} or the T_{2g} octahedral absorption (Table 1; Figures 1—3, 7, and 8).

Following the method of Orgel [24] it is found that, if LL is bidentate and conjugated in the *cis*-complexes $Co(NH_3)_4L_2^{3+}$, the degeneracy of the C_{2v} orbitals $d_{x'y'}$ and $d_{y'z'}$ of the co-ordinate frame (III) is split, and the A_2 and the B_2 components of both the T_{1g} and the T_{2g} cobalt(III) state are resolved. The splitting depends [24] upon the symmetry of the π-orbitals of the conjugated ligand LL. The lowest unoccupied π-orbital of the oxalate dianion, for example, is symmetric with respect to the mirror plane which bisects the oxalate chelate ring in $Co(NH_3)_4(ox)^+$ or $Co(en)_2(ox)^+$, and this ligand π-orbital conjugates only with the $d_{y'z'}$ orbital of the cobalt(III) ion, so that the $d_{x'y'}$ orbital has the higher energy. The π and σ perturbations due to the conjugated oxy-ligand in (+)-$Co(en)_2(CO_3)^+$ and (+)-$Co(en)_2(ox)^+$ are additive for the T_{2g} octahedral transition, producing three well resolved circular dichroism bands, but these perturbations are opposed for the corresponding T_{1g} transition, and only one circular dichroism band is observed owing to the smaller energy separations between three components (Table 1; Figures 4 and 5).

The present assignment of the circular dichroism bands exhibited by the *cis*-complexes $Co(en)_2L_2^{2+}$ is supported in a number of the cases studied by the observed changes in band area due to outer-sphere co-ordination. It has been found [25] that polarisable anions, particularly trigonal or tetrahedral oxyanions such as phosphate, thiosulphate, selenite, or carbonate, enhance and diminish, respectively, the band area of the A_2 and the E_a circular dichroism absorption of the d^3 and d^6 transition metal trisdiamine complexes when added to aqueous solutions of the perchlorate of the complex. The effect is independent of the metal ion, and it provides an empirical method for the identification of the circular dichroism bands due to the A_2 and the E_a transitions in the trisdiamine series of metal complexes.

The effects of polarisable oxyanions upon the circular dichroism band areas of the *cis*-series of bisdiamine cobalt(III) complexes are generally smaller in magnitude since the corresponding rotational strengths are of mixed A_2 and E_a trigonal parentage (eqns. 2—8). However, the dominant A_2 or E_a trigonal parentage of a particular circular dichroism band given by a *cis*-$Co(en)_2L_2^{3+}$ complex should be manifest in the outer-sphere co-ordination effect upon the area of that band.

Of the various oxyanions investigated, selenite is found to be particularly convenient, producing large effects, without precipitation of the selenite salt of the complex ion, when added in low to moderate (0·2M) concentrations to 0·01M-solutions of the complex. The effects of such an addition upon the areas of the corresponding circular dichroism bands of *cis*-(+)-$Co(en)_2(NH_3)^{3+}$ and (+)-$Co(en)_3^{3+}$ are of the same sign and relative magnitude (Figure 1), confirming that the major and the minor long-wavelength circular dichroism bands of *cis*-(+)-$Co(en)_2(NH_3)_2^{3+}$ are due to transitions with predominant parentage in the E_a and A_2 transitions, respectively, of (+)-$Co(en)_3^{3+}$.

In the limiting C_{2v} case of *cis*-(+)-$Co(en)_2(CN)_2^+$ where the parent trigonal rotational strengths $R[A_2]$ and $R[E_a]$ contribute equally, or nearly so, to each of the two long-wavelength circular dichroism bands (eqn. 8 and eqn. 7 with $c = 1/\sqrt{3}$), the effect of selenite upon the band areas is small (Figure 2), as also in $Co(en)_2L_2^{3+}$ with LL a bidentate

[24] L. E. Orgel, *J.*, 1961, 3683.
[25] S. F. Mason and B. J. Norman, *Proc. Chem. Soc.*, 1964, 339.

ligand, where $R[A_2]$ and $R[E_a]$ contribute equally to the single circular dichroism band in the region of the octahedral T_{1g} absorption (Figure 5). The major of the two long-wavelength circular dichroism bands of *cis*-(+)-$Co(en)_2Cl_2^+$ (Figure 3) and *cis*-(−)-$Co(en)(N_3)_2^+$ (Figure 7) is reduced in area by the addition of selenite as required by the dominant contribution of the trigonal parent $R[E_a]$ to this band. However the minor circular dichroism band of *cis*-(+)-$Co(en)_2Cl_2^+$ is but little affected by the addition of selenite and does not show the increase in band area expected (Figure 3). The more labile of the *cis*-complexes $Co(en)_2L_2^{3+}$, notably, L = Cl^-, H_2O, and LL = CO_3^{2-}, ox^{2-}, react with polarisable anions, requiring an extrapolation of the outer-sphere co-ordination effect to zero time, and in the case of (+)-$Co(en)_2(H_2O)_2^{3+}$ the rate of reaction is too fast to permit a reliable extrapolation. The results for *cis*-(+)-$Co(en)_2(NO_2)_2^+$ are inconclusive, the addition of 0·2M- and of 1·5M-selenite producing contrary effects (Figure 8).

In general the outer-sphere co-ordination effect is a less reliable guide to the assignment of the circular dichroism bands of the complexes *cis*-$Co(en)_2L_2^{3+}$ than the frequency-displacement and the relative band-area criteria described above, except for the cases near to the D_3 limit where the ligand L is an amine.

The stereochemical configuration recorded (Table 1) for each of the *cis*-bisdiamine complexes is specified by these criteria and the relationship proposed above between the sign of the circular dichroism band with the dominant E_a trigonal parentage and the handedness of the chelate rings about the metal ion. The relative configurations assigned (Table 1) are in general agreement with those previously derived from the sign of the long-wavelength Cotton effect [5,23,26-28] or from sequences of chemical interconversions.[27-29] The optical rotatory dispersion curves of the complexes *cis*-$Co(en)_2L_2^{3+}$ show in general a single anomaly in the visible region [26,27] and they do not distinguish the separate Cotton effects due to the components of the octahedral T_{1g} transition. The sign of the anomaly in the dispersion curve reflects the sign of the major long-wavelength circular dichroism band, which is of dominant E_a trigonal parentage in the complexes *cis*-$Co(en)_2L_2^{3+}$, and the present identification of the individual Cotton effects arising from the components of the octahedral T_{1g} transition supports the previous assignments of stereochemical configuration in this series.[5,23,26-29]

However, the sign of neither the anomalous rotatory dispersion [5,26-28] nor the major long-wavelength circular dichroism band [23] is a general criterion for the assignment of configuration to a dissymmetric metal complex. The inequality of eqn. (9) holds [2] for the majority of the resolved trigonal d^3 and d^6 metal complexes, but the converse inequality $|R[A_2]| > |R[E_a]|$ obtains [2] for (+)-$Rh(-pn)_3^{3+}$ and (−)-$Cr(mal)_3^{3-}$. In the case of the latter and related bis-chelate complexes the major circular dichroism band in the region of the octahedral T_{1g} absorption, and the corresponding anomalous rotatory dispersion, have a sign determined by that of the rotational strength of the A_2, and not the E_a, trigonal transition.

The classical study by Mathieu [23] of the circular dichroism of the bisdiamine complexes extended to the series *cis*-$Co(en)_2L'L^{3+}$, which with L $\neq$ L′ are formally devoid of symmetry elements. However, the complexes *cis*-$Co(en)_2(NH_3)L^{3+}$ approximate to C_{4v} symmetry if the perturbation due to the ligand L is stronger than that due to chelation. In C_{4v} metal complexes the octahedral T_{1g} transition breaks down into components with A_2 and E symmetry, which are, respectively, undisplaced and displaced by $\delta/4$ from the energy of the parent hexa-ammine transition.[19] For the complexes *cis*-$Co(en)_2(NH_3)L^{3+}$ near to the C_{4v} limit the rotational strengths of the A_2 and the E components of the octahedral T_{1g} transition are given by the right-hand side of eqn. (8), and eqn. (7) with $c = 1/\sqrt{3}$, respectively. These theoretical requirements are in agreement with the circular dichroism

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spectra of Mathieu.[23] The complexes *cis*-$Co(en)_2(NH_3)L^{3+}$ with L = Cl^-, Br^-, or H_2O give [23] two circular dichroism bands with the same sign and an approximate band area ratio of 2 : 1. The minor circular dichroism band lies nearly at the same frequency as the long-wavelength absorption band of *cis*-$Co(en)_2(NH_3)_2{}^{3+}$, whereas the major circular dichroism band is the further displaced from that frequency the larger is the separation between the ligand L and the amines in the spectrochemical series.[23] Hence, the minor and the major long-wavelength circular dichroism bands of *cis*-$Co(en)_2(NH_3)L^{3+}$ are due, respectively, to the A_2 and the E components of the octahedral T_{1g} transition.

Mathieu showed [23] that the isomers of *cis*-$Co(en)_2L'L^{3+}$ with a positive major circular dichroism band, which were thus assigned the same absolute configuration as (+)-$Co(en)_3{}^{3+}$, gave, in general, the less-soluble (+)-α-bromocamphorsulphonate salt. However, the less-soluble isomer of *cis*-$Co(en)_2(NH_3)(NO_2)^{2+}$ was found [23] to give a negative circular dichroism band in the region studied, covering some two-thirds of the wavelength range spanned by the long-wavelength absorption band, and it was concluded [23] that Werner's solubility criterion [30] for relative configuration was of limited application.

The conclusion of Mathieu is supported by the present work. The less-soluble (+)-α-bromocamphorsulphonate of $Co(en)_2(phen)^{3+}$ gives [31] a negative long-wavelength circular dichroism band, and (+)-$Co(en)_2(CO_3)^+$ and *cis*-(+)-$Co(en)_2(Cl)_2{}^+$, which have the same configuration, form the less-soluble salt [29] with (+)- and with (−)-$Co(ox)_2(en)^-$, respectively (Table 1). In the latter case the salts formed are not isomorphous.[29] Similarly, (+)-$Co(en)_3{}^{3+}$ and (−)-$Co(en)_2(bipy)^{3+}$ with antipodal configurations are the isomers forming the less-soluble salt with (−)-$Co(ox)_3{}^{3-}$, and (+)-$Co(en)_2(CO_3)^+$ and (+)-$Co(en)_3{}^{3+}$ with the same configuration form, respectively, the more-soluble and the less soluble salt with antimonyl (+)-tartrate (Table 1).

Experimental

Materials.—Salts of *cis*-(+)-$Co(en)_2(NH_3)_2{}^{3+}$, (+)-$Co(en)_2(CO_3)^+$, (+)-$Co(en)_2(ox)^+$, (+)- and (−)-$Co(-pn)_2(ox)^+$, and (+) $Co(en)_2(acac)^{2+}$ were kindly provided by Dr. A. M. Sargeson,[5,27,29] and cis-(+)-$[Cr(en)_2Cl_2]Cl,H_2O$ by Dr. Th. Bürer.[26] Each of the remaining optical isomers used was prepared as described in the accompanying reference: *cis*-(+)-$[Co(en)_2Cl_2]I$,[29] $[\alpha]_D = +660°$; *cis*-(+)-$[Co(en)_2(NO_2)_2]Cl$,[32] $[\alpha]_D = +47°$; *cis*-(+)-$[Co(en)_2(H_2O)_2](NO_3)_3$,[29] $[\alpha]_{546} = +300°$; *cis*-(+)- and -(−)-$[Co(en)_2(N_3)_2]NO_3$,[33] $[\alpha]_D = \pm 167°$; *cis*-(+)-$[Co(en)_2(CN)_2]$ (+)-α-bromocamphorsulphonate,[34] $[M]_D = +66°$. $[Co(en)_2bipy]I_3$ was obtained by the method described for the preparation [35] of the corresponding 1,10-phenanthroline complex, and was resolved [36] with (−)-$Co(ox)_3{}^{3-}$, $[M]_D = +60°$.

Spectra.—These were obtained for the complex perchlorate at <0·01M in water and in solutions of sodium selenite up to 1·5M. Circular dichroism spectra were measured with a Jouan Dichrograph and with a circular dichroism spectrophotometer previously described.[37] Optical rotations were measured with a Bellingham and Stanley spectropolarimeter, and absorption spectra with an Optica double-beam grating spectrophotometer. The unpolarised and the circularly polarised light-absorption indices are the decadic molar extinction coefficient $[\varepsilon = (1/cl) \log (I_0/I)]$ in units of l. mole^{-1} cm.$^{-1}$.

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