519. *Optical Rotatory Power of Co-ordination Compounds. Part III.* The Absolute Configurations of Trigonal Metal Complexes*

By A. J. McCaffery, S. F. Mason, and (in part) R. E. Ballard

Circular dichroism spectra are reported for trigonal chelate complexes of transition-metal ions with diamine, dicarboxylic acid, and β-dicarbonyl ligands, in solution and, where possible, in a uniaxial crystal. The optical rotatory power associated with the long-wavelength absorption is found to consist, in general, of two circular dichroism bands with opposed signs, due to electronic transitions polarised, respectively, parallel and perpendicular to the three-fold axis of the complex. The sign of each of these two bands is correlated with the stereochemical chirality of the complex presented along the polarisation direction of the transition giving the particular circular dichroism absorption, a positive and a negative optical rotatory power being associated with a right-handed and a left-handed helical stereochemistry, respectively. By means of this optical principle, the isomers with the same absolute configuration as (+)-$Co(en)_3^{3+}$ are found to be the trigonal diamine complexes with the less-soluble halide-(+)-tartrate salt and the trigonal dicarboxylic acid complexes forming the less-soluble (−)-strychnine salt.

The configurations of a wide variety of organic compounds have been related optically,[1] and the relative configurations, checked by chemical interconversions, have been placed on an absolute basis by reference to optical isomers with absolute configurations established by *X*-ray diffraction. The relative and absolute configurations of dissymmetric co-ordination compounds are established less extensively and with less certainty, however, and for metal complexes there is known as yet no satisfactory generalisation analogous to the Octant Rule[2] for optically active carbonyl compounds. The major limitations to the assignment of configuration in the series of co-ordination compounds are the limited number of metal complexes available with absolute configurations determined by *X*-ray diffraction, the paucity of interconversion reactions—as yet, no two dissymmetric trigonal complexes have been interrelated chemically, for example—and the complexity of the transition-metal ion chromophore. The $d \longrightarrow d$ transitions of octahedral metal

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

[1] W. Klyne, " Stereochemical Correlations," R.I.C. Monograph, No. 4, 1962; C. Djerassi, " Optical Rotatory Dispersion," McGraw-Hill, New York, 1960.

[2] W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne, and C. Djerassi, *J. Amer. Chem. Soc.*, 1961, **83**, 4013.

complexes are invariably degenerate, and it is necessary to identify at least one of the components into which these transitions are split in a dissymmetric co-ordination compound, in order to apply the principle that two related optically active molecules have the same absolute configuration if they give a Cotton effect of the same sign in the absorption wavelength region of an electronic transition common to both molecules.

The present work reports the measurement of the absorption and the circular dichroism spectra of a number of dissymmetric trigonal complexes in solution (Table 1; Figures

TABLE 1

The absorption and circular dichroism spectra, in aqueous solution, of d^3 and d^6 trigonal metal complexes, due to the spin-allowed $d \longrightarrow d$ electronic transitions. Square brackets denote tentative assignments. Values in italics refer to inflexions

Complex[a]	Isomer	Absorption	Circular dichroism		Transition	Confign.	Ref.
		$\lambda_{max.}$ (Å) ($\varepsilon_{max.}$)	$\lambda_{max.}$ (Å)	$(\varepsilon_l - \varepsilon_r)_{max.}$			
$(+)$-$Co(en)_3{}^{3+}$	*b*	4690(84)	4930	+1·89	E_a	$M(C_3)$	*f*
			4280	−0·17	A_2		
		3400(74)	3510	+0·25	E_b		
$(+)$-$Co(+\ pn)_3{}^{3+}$ ...	*c*	4680(96)	4930	+1·95	E_a	$M(C_3)$	*g*
			4390	−0·58	A_2		
		3400(90)	3480	+0·20	E_b		
$(+)$-$Cr(en)_3{}^{3+}$	*b*	4600(74)	4560	+1·36	E_a	$M(\mathrm{C}_3)$	*g*
		3530(65)	3500	−0·05	E_b		
$(-)$-$Cr(-\ pn)_3{}^{3+}$ ...	*c*	4600(71)	4700	−1·30	E_a	$P(C_3)$	*g*
			4080	+0·06	A_2		
		3530(56)	3660	−0·06	E_b		
$(-)$-$Rh(en)_3{}^{3+}$	*b*	3060(251)	3200	+2·0	E_a	$M(C_3)$	*g*
			2870	−0·1	A_2		
		2570(246)	2580	+0·8	E_b		
$(+)$-$Rh(-\ pn)_3{}^{3+}$ ...	*c*	3030(252)	3230	−0·72	E_a	$P(C_3)$	*g*
			2900	+1·25	A_2		
		2550(215)	2530	−0·5	E_b		
$(-)$-$Ir(en)_3{}^{3+}$	*b*	3100(500)	3150	+0·4	E_a	$M(C_3)$	*h*
$(-)$-$Co(ox)_3{}^{3-}$.........	*d*	6020(153)	6170	+3·30	[E_a]	$M(C_3)$	*g*
		4220(204)	4460	+0·26			
			4120	−0·26	[E_b]		
			3770	+0·21			
$(+)$-$Co(+\ tart)_3{}^{3-}$ ...	*c*	6400(168)	6200	+4·6	[E_a]	[$M(C_3)$]	*g*
		4460(215)	4300	−0·8	[E_b]		
$(+)$-$Cr(ox)_3{}^{3-}$	*d*	5710(74)	6300	−0·58	A_2	$M(C_3)$	*g*
			5520	+2·83	E_a		
		4220(97)	4150	−0·56	E_b		
$(+)$-$Cr(+\ tart)_3{}^{3-}$ ...	*c*	5950(66)	6625	−0·88	[A_2]	[$M(C)_3$]	*i*
			5840	+3·77	[E_a]		
		4350(81)	4330	−1·24	[E_b]		
$(-)$-$Cr(mal)_3{}^{3-}$	*d*	5750(30)	6200	+0·07	E_a	$M(C_3)$	*g*
			5550	−0·20	A_2		
		4280(24)	4200	+0·04	E_b		
$(+)$-$Rh(ox)_3{}^{3-}$	*d*	4020(330)	4000	+2·85	E_a	$M(C_3)$	*g*
$(+)$-$Ir(ox)_3{}^{3-}$	*d*	4400(100)	4600	+1·0	[E_a]	[$M(C_3)$]	*h*
$(-)$-$Co(thiox)_3{}^{3-}$ ...	*e*	*5700(450)*	6350	+0·2	[A_2]	[$P(C_3)$]	*g*
			5400	−2·8	[E_a]		
		4600(1800)	3800	+16·2			
$(+)$-$Rh(thiox)_3{}^{3-}$ ...	*e*	*4000(6000)*	4600	+0·5	[A_2]	[$P(C_3)$]	*g*
			4150	−2·0	[E_a]		
		3600(7000)	3440	+8·8			
$(+)$-$Co(+\ hmc)_3$......	*c*	6100(174)	7000	−0·4	A_2	$M(C_3)$	*g*
			6100	+5·2	E_a		
		4400(530)	4600	−5·5	[E_b]		
$(+)$-$Cr(+\ hmc)_3$......	*c*	5650(67)	6400	−0·7	A_2	$M(C_3)$	*g*
			5450	+4·2	E_a		
		4700(187)	4720	+0·7	[E_b]		

[a] The abbreviations used are: en, ethylenediamine; pn, propylenediamine; ox, oxalate; thiox, thio-oxalate; tart, tartrate; mal, malonate; and hmc, hydroxymethylenecamphor. [b] The isomer forming the less-soluble chloro-(+)-tartrate salt. [c] The more-stable isomer. [d] The isomer forming the less-soluble (−)-strychnine salt. [e] The isomer forming the less-soluble (+)-*cis*-$Co(en)_2(NO_2)_2{}^+$ salt. [f] A. J. McCaffery and S. F. Mason, *Mol. Phys.*, 1963, **6**, 359. [g] Present work. [h] J. P. Mathieu, *J. Chim. phys.*, 1936, **33**, 78. [i] A. J. McCaffery and S. F. Mason, *Trans. Faraday Soc.*, 1963, **59**, 1.

TABLE 2

The circular dichroism of d^3 and d^6 trigonal metal complex ions orientated in uniaxial crystals, measured with the radiation propagated along the three-fold rotation axis of the complex. Values in italics refer to an inflexion

Complex-ion [a]	Crystal	$\lambda_{max.}$ (Å)	$(\varepsilon_l - \varepsilon_r)_{max.}$	Transition	Ref
(+)-Co(en)$_3^{3+}$	2[(+)-Co(en)$_3$Cl$_3$],NaCl,CH$_2$O	4750	+23	E_a	*b*
		3450	+0·9	E_b	
(−)-Rh(en)$_3^{3+}$	(−)-Rh(en)$_3$Cl$_3$,H$_2$O	<3250	>+15	E_a	*c*
(−)-Co(ox)$_3^{3-}$	NaMgAl(ox)$_3$,9H$_2$O	6200	+39	E_a	*d*
		4300	+3·5	E_b	
(+)-Cr(ox)$_3^{3-}$	NaMgAl(ox)$_3$,9H$_2$O	5610	+11	E_a	*c*
		4100	−0·5	E_b	
(+)-Rh(ox)$_3^{3-}$	NaMgAl(ox)$_3$,9H$_2$O	3950	+43	E_a	*c*
		3330	*+10*	E_b	

[a] The abbreviations used are as in Table 1. [b] A. J. McCaffery and S. F. Mason, *Mol. Phys.*, 1963, **6**, 359. [c] Present work. [d] A. J. McCaffery and S. F. Mason, *Proc. Chem. Soc.*, 1962, 388; reported values corrected in the present work.

1 and 2). Where possible, circular dichroism measurements have been made with the complex metal ion orientated in a crystal having a known structure (Table 2), in order to relate the configurations of different complexes by identifying the sign of the Cotton effect associated with an electronic transition of known symmetry. Preliminary results and conclusions have been described previously.[3,4]

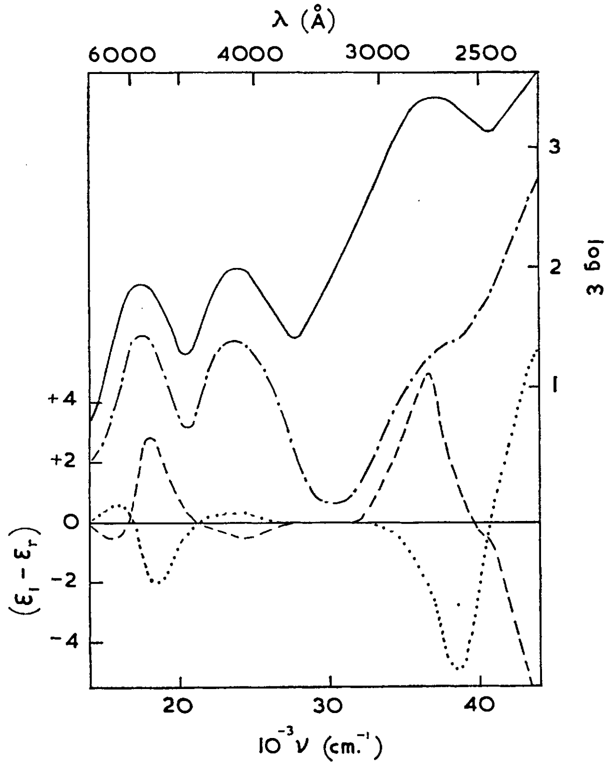

FIGURE 1. The electronic absorption spectrum ——— of K$_3$Cr(ox)$_3$, and — · — · — of K$_3$Cr(mal)$_3$, and the circular dichroism absorption — — — of (+)-Cr(ox)$_3^{3-}$, and · · · of (−)-Cr(mal)$_3^{3-}$. The left-hand ordinate scale gives the absolute magnitude of the circular dichroism of (+)-Cr(ox)$_3^{3-}$, and the circular dichroism of (−)-Cr(mal)$_3^{3-}$ (see Table 1) multiplied by a factor of ten

The dissymmetric trigonal complexes † with absolute configurations determined by *X*-ray diffraction are (+)-Co(en)$_3^{3+}$ as the chloride [5] and the bromide [6] and (−)-Co(−pn)$_3^{3+}$

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

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

[4] A. J. McCaffery and S. F. Mason, *Proc. Chem. Soc.*, 1962, 388.

[5] K. Nakatsu, M. Shiro, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Japan*, 1957, **30**, 158.

[6] K. Nakatsu, *Bull. Chem. Soc. Japan*, 1962, **35**, 832.

as the bromide.[7] The absolute configuration of (+)-Co(en)$_3{}^{3+}$ has been conventionally termed,[5-9] D from the sign of the rotation at the sodium yellow lines, and Λ,[10] from the left-handed chirality (I) of the complex. A stereochemical basis is desirable for the description of configuration,[11] and, in the case of trigonal metal complexes, a reference frame for the specification of handedness is necessary. In all dissymmetric molecules belonging to the dihedral point-groups D_p, the stereochemical chirality parallel to the principal axis C_p is opposed to that presented along each of the p two-fold axes perpendicular to C_p. Thus, (+)-Co(en)$_3{}^{3+}$, which belongs to the point-group D_3, has the form of a left-handed helical screw (I) when viewed along the three-fold axis C_3, but if viewed along any of the two-fold axes C_2, it presents the appearance (II) of a right-handed helical segment. A full stereochemical specification of the absolute configuration of (+)-Co(en)$_3{}^{3+}$ is $M(C_3),P(C_2)$, M (minus) and P (plus) being used to designate † a left- and a right-handed helical form, respectively, about the appropriate symmetry axis, although $M(C_3)$ implies $P(C_2)$ and either description specifies the configuration.

The X-ray-diffraction study[7] of (−)-Co(−pn)$_3$Br$_3$ indicates that this complex has the configuration $P(C_3)$, confirming the prediction[12] of Corey and Bailar who showed, by the methods of conformational analysis, that (−)-Co(−pn)$_3{}^{3+}$ has a configuration around the cobalt ion enantiomeric with that of (+)-Co(en)$_3{}^{3+}$, and is more stable than (+)-Co(−pn)$_3{}^{3+}$ by 1·8 kcal./mole. Experimentally it has been found[13] from equilibration studies that (−)-Co(−pn)$_3{}^{3+}$ is more stable thermodynamically by 1·6 kcal./mole than (+)-Co(−pn)$_3{}^{3+}$.

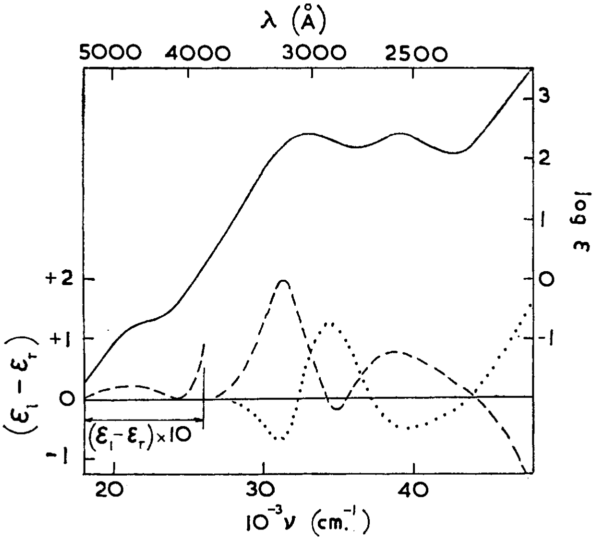

FIGURE 2. The electronic absorption spectrum ——— of Rh(en)$_3$Cl$_3$, and the circular dichroism absorption — — — of (−)-Rh(en)$_3{}^{3+}$, and · · · · of (+)-Rh(−pn)$_3{}^{3+}$

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† The use of M and P to describe the chirality, respectively, of a left- and a right-handed helical or propellor-shaped structure follows an unpublished recommendation of Cahn, Ingold, and Prelog (*Angew. Chem.*, 1965, to be published). The alternative symbols, Λ and Δ, may be confused one with the other, whilst L and D, or S and R, have established conventional significances[11] which are not generally appropriate for the description of helical chirality.

[7] Y. Saito, H. Iwasaki, and H. Ota, *Bull. Chem. Soc. Japan*, 1963, **36**, 1543.

[8] T. E. MacDermott and A. M. Sargeson, *Austral. J. Chem.*, 1963, **16**, 334.

[9] R. D. Gillard and G. Wilkinson, *J.*, 1964, 1368.

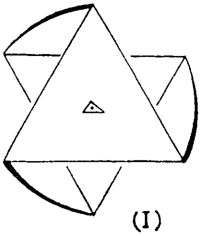
[10] T. S. Piper, *J. Amer. Chem. Soc.*, 1961, **83**, 3908.

[11] R. S. Cahn and C. K. Ingold, *J.*, 1951, 612; R. S. Cahn, C. K. Ingold, and V. Prelog, *Experientia*, 1956, **12**, 81; *Angew. Chem.*, 1965, to be published.

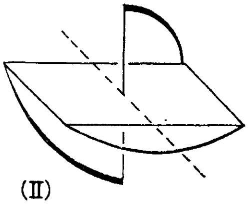
[12] E. J. Corey and J. C. Bailar, *J. Amer. Chem. Soc.*, 1959, **81**, 2620.

[13] 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.

Although the ratio of the products formed in the reaction between (—)-propylenediamine and transition-metal ions is probably controlled kinetically rather than thermodynamically, it is assumed in the present work that the more-abundant isomer, namely, (—)-Cr(—pn)$_3^{3+}$ and (+)-Rh(—pn)$_3^{3+}$, like (—)-Co(—pn)$_3^{3+}$, has the configuration $P(C_3)$. In principle, the absolute configuration of the (+)-tartrate and (+)-hydroxymethylenecamphor complexes of the transition-metal ions may be related to that of the ligand, but as yet, insufficient structural information is available for the evaluation of the non-bonding interactions in isomeric complexes of these types.



(I)



(II)

The absolute configurations, established by *X*-ray diffraction or inferred by the methods of conformational analysis, for the d^3 and d^6 diamine co-ordination compounds are systematically related to the sign of the circular dichroism bands given by these complexes in the wavelength region of the spin-allowed $d \longrightarrow d$ band of lowest energy. Previous studies [14] and the present results indicate that, as expected theoretically, this band of the several $d \longrightarrow d$ absorptions is associated with the major optical rotatory power, which consists in general of two circular dichroism bands with opposed signs (Figures 1 and 2). The band area of a circular dichroism absorption provides an experimental measure of the rotational strength, *R*, which represents theoretically the scalar product of the electric moment, ρ, and the magnetic moment, μ, of the electronic transition responsible for the absorption

$$R_{ab} = (\rho_{ab}\mu_{ba}) \qquad (1)$$

In octahedral complexes, the spin-allowed transition of lowest energy, with the symmetry T_{1g} in the group O_h, has a magnetic moment [15] of $\sqrt{12}\beta_M$ and $\sqrt{24}\beta_M$ for d^3 and strong-field d^6 metal ions, respectively, β_M being the Bohr magneton, whereas the higher-energy transition with T_{2g} symmetry has a zero magnetic moment. The symmetry of a transition denotes the direct product of the irreducible representations of the electronic states connected by the transition, so that, for example, the excitations $^4A_{2g} \longrightarrow {}^4T_{2g}$ of chromium(III) and $^1A_{1g} \longrightarrow {}^1T_{1g}$ of cobalt(III) are both T_{1g} transitions.

The octahedral T_{1g} transition is broken down in the corresponding trigonal complex, which belongs to the group D_3, into a non-degenerate 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 of *E* symmetry, designated E_a, with moments directed perpendicular to the C_3 axis. Similarly, the octahedral T_{2g} transition is broken down, in the dihedral complex, into a forbidden component of A_1 symmetry and a doubly-degenerate component (E_b) polarised perpendicular to the C_3 axis. Each of the $d \longrightarrow d$ transitions allowed in the dihedral complex acquires an electric moment due to the trigonal field, but the magnetic moment of the octahedral T_{1g} transition is shared largely by the A_2 and the E_a components in the ratio $1 : \sqrt{2}$. Accordingly, the dihedral A_2 and E_a transition have each a large first-order rotational strength, whereas the E_b transition acquires only a small second-order rotational strength by mixing with other transitions of *E* symmetry, notably E_a. A pair of related transitions with moments, respectively, parallel (A_2) and perpendicular (E_a) to the principal axis of a dihedral metal complex should have rotational strengths of

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[14] S. F. Mason, *Quart. Rev.*, 1963, **17**, 20.

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

equal magnitude and opposed sign,[16-20] owing to the opposed stereochemical chiralities of the complex parallel (I) and perpendicular (II) to the three-fold axis. If the complex ions are randomly orientated, the rotational strengths $R(A_2)$ and $R(E_a)$ mutually cancel to a degree depending upon the energy interval between the two transitions.[21] If, however, the complex-ions are regularly orientated in a crystal with their three-fold axes parallel to the optic axis of the crystal, $R(E_a)$ may be measured directly, as radiation propagated along the optic axis of the crystal can give rise only to electronic transitions of E symmetry.[22]

The experimental measurements (Tables 1 and 2; Figures 1 and 2) largely conform to these expectations. In general, the trigonal metal complexes in solution give two circular dichroism bands with opposed signs, due to the A_2 and the E_a transitions, under the long-wavelength unpolarised absorption, and a single circular dichroism band, due to the E_b transition, at shorter wavelengths (Table 1). When orientated in a uniaxial crystal, however, the trigonal complexes give, in the region of the long-wavelength band, a single circular dichroism absorption which has a band area of an order of magnitude larger than that of the corresponding absorption observed in solution (Tables 1 and 2), suggesting that, in the randomly orientated complex, $R(A_2)$ and $R(E_a)$ mutually cancel to within *ca.* 10 per cent. In solution, the A_2 and the E_a circular dichroism bands are residual wing absorptions, the extensive cancellation accounting for the large frequency interval (~3000 cm.⁻¹) between the two dichroism bands, compared with the difference between the A_2 and E_a transition energies (Table 3) given by the corresponding crystal spectra measured with plane-polarised radiation.[23-25]

TABLE 3

The frequency difference, $\nu(E_a) - \nu(A_2)$, between the spin-allowed transitions of lowest energy, and the intensity ratio, $I(A_2)/I(E_a)$, obtained from the plane-polarised crystal spectra of trigonal metal complexes

Complex [a]	$\nu(E_a) - \nu(A_2)$ (cm.$^{-1}$)	$I(A_2)/I(E_a)$	Ref.
$Co(en)_3^{3+}$	Small	1·38	*b*
$Cr(en)_3^{3+}$	Small	1·47	*b*
$Co(ox)_3^{3-}$	−150	1·33	*b*
$Cr(ox)_3^{3-}$	+300	1·46	*b*
$Cr(mal)_3^{3-}$	−180	1·4	*c*
$Co(acac)_3$	+800	1·02	*b*
$Cr(acac)_3$	+800	1·50	*b*

[a] The abbreviations used are as in Table 1, with acac = acetylacetonate. [b] A. G. Karipides and T. S. Piper, *J. Chem. Phys.*, 1964, **40**, 674. [c] W. E. Hatfield, *Inorg. Chem.*, 1964, **3**, 605.

A comparison of the crystal and the solution circular dichroism spectra of (+)-$Co(en)_3^{3+}$ and (−)-$Rh(en)_3^{3+}$ shows (Tables 1 and 2) that the E_a transition has a positive rotational strength and lies at a longer wavelength than the A_2 transition in these complexes. (+)-Co(+pn)$_3^{3+}$, which, like (+)-$Co(en)_3^{3+}$, has the $M(C_3)$ configuration,[7] gives similarly a positive circular dichroism band at the longer wavelength, whereas (−)-Cr(−pn)$_3^{3+}$ and (+)-Rh(−pn)$_3^{3+}$, which have the enantiomeric $P(C_3)$ configuration,[12] give a negative circular dichroism band at the longer wavelength (Table 1). These observations suggest that the configuration of a trigonal metal complex is related to the sign of the rotational

[16] S. Sugano, *J. Chem. Phys.*, 1960, **33**. 1883.
[17] N. K. Hamer, *Mol. Phys.*, 1962, **5**, 339.
[18] H. Poulet, *J. Chim. phys.*, 1962, **59**, 584.
[19] T. S. Piper and A. Karapides, *Mol. Phys.*, 1962, **5**, 475; *J. Chem. Phys.*, 1964, **40**, 674.
[20] A. Liehr, *J. Phys. Chem.*, 1964, **68**, 665.
[21] T. Burer, *Helv. Chim. Acta*, 1963, **46**, 242, 2388.
[22] A. J. McCaffery and S. F. Mason, *Mol. Phys.*, 1963, **6**, 359.
[23] S. Yamada and R. Tsuchida, *Bull. Chem. Soc. Japan*, 1960, **33**, 98.
[24] T. S. Piper and R. L. Carlin, *J. Chem. Phys.*, 1960, **33**, 608; 1961, **35**, 1809; 1962, **36**, 3330; *Inorg. Chem.*, 1963, **2**, 260.
[25] W. E. Hatfield, *Inorg. Chem.*, 1964, **3**, 605.

strength of the E_a transition, $R(E_a)$ being positive for the $M(C_3)$ configuration (I) and negative for the enantiomeric $P(C_3)$ configuration. For a given complex, $R(A_2)$ and $R(E_a)$ have opposite signs, and in general each rotational strength has the same sign as the stereochemical chirality which is presented when the complex is viewed along the polarisation direction of the transition. The $M(C_3)$ configuration (I), for example, has the $P(C_2)$ stereochemical chirality (II), and the A_2 transition polarised parallel to the C_3 axis has a negative (M) rotational strength, whereas the E_a transition polarised perpendicular to the C_3 axis has a positive (P) rotational strength. According to both the classical and the quantum-mechanical theory, an electron displaced along a right-handed and along a left-handed helical path has, respectively, a positive and a negative optical rotatory power.

Application of the principle that the stereochemical configuration of a trigonal metal complex is related to the signs of the rotational strengths of the A_2 and the E_a transitions requires general methods for the identification of the circular dichroism band due to the one or the other of these transitions. Three such methods are available, namely, the measurement of the axial circular dichroism of the complex-ion orientated in a uniaxial crystal, and the determination of the frequencies or the intensity-ratio of the A_2 and the E_a transitions given by the complex orientated in a crystal, which is not necessarily uniaxial, using plane-polarised radiation.

Another method, specific for the diamine co-ordination compounds, is based upon the observation that, in the presence of tetrahedral or trigonal oxyanions, such as phosphate or sulphite, the areas of the A_2 and the E_a circular dichroism bands in the spectra of the trisethylenediamine or trispropylenediamine complexes of cobalt(III), chromium(III), or rhodium(III) are, respectively, enhanced and diminished, owing to charge-transfer interaction within the ion-pair.[26] The assignments inferred from the gegen-ion effect in solution agree in all cases with those obtained by the general methods based upon crystal measurements.

The crystal circular dichroism of a trigonal complex gives directly the sign and the magnitude of the rotational strength of the electronic transitions with E symmetry, notably E_a, and for all of the complexes studied (Table 2), $R(E_a)$ is positive, indicating that these compounds have the $M(C_3)$ configuration (Table 1). The A_2 and E_a transition frequencies (Table 3), obtained [23-25] from the plane-polarised crystal spectrum of a given complex, identify the transition responsible for each of the two circular dichroism bands shown by that complex in the region of the long-wavelength absorption band in solution (Table 1). This method indicates that the shorter-wavelength circular dichroism band of (+)-$Cr(ox)_3^{3-}$ in solution is due to the E_a transition, in agreement with the assignment based on the circular dichroism of the complex orientated in a uniaxial crystal, but that the corresponding transition gives rise to the longer-wavelength circular dichroism band of (—)-$Cr(mal)_3^{3-}$ (Tables 1 and 3). The circular dichroism band due to the E_a transition is positive in both cases, indicating that (+)-$Cr(ox)_3^{3-}$ and (—)-$Cr(mal)_3^{3-}$ have the $M(C_3)$ configuration. A comparison of the general form of the circular dichroism spectra given by the two complexes (Figure 1) suggests, on the contrary, that (+)-$Cr(ox)_3^{3-}$ and (—)-$Cr(mal)_3^{3-}$ have enantiomeric configurations. The results for these two complexes illustrate that the comparison of the general form of Cotton-effect curves is an unreliable guide to the assignment of relative configuration in cases where the major optical rotatory power is due to two or more electronic transitions which are degenerate in the corresponding symmetric molecule, *e.g.*, the corresponding octahedral chromium(III) complex in the present case; this is particularly so where the frequency differences between the components, into which the degenerate transition is split in the dissymmetric molecule, are small and variable in sign.

The frequency differences between the A_2 and the E_a transitions are relatively large in

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[26] S. F. Mason and B. J. Norman, *Proc. Chem. Soc.*, 1964, 339.

the trisacetylacetonate complexes of chromium(III) and cobalt(III) (Table 3), and it is assumed that similar splittings obtain in the corresponding complexes derived from the analogous β-dicarbonyl ligand, (+)-hydroxymethylenecamphor (+hmc). These frequency differences indicate that $R(E_a)$ is positive for the more-stable isomers, (+)-Cr(+hmc)$_3$ and (+)-Co(+hmc)$_3$, so that these complexes have the $M(C_3)$ configuration (Tables 1 and 3).

The third method of identifying the solution circular dichroism bands due to the A_2 and the E_a transition depends upon the deviations observed experimentally from the theoretical sum rule,[16-20] that is,

$$R(A_2) + R(E_a) = 0 \qquad (2)$$

Since the magnetic moment of the octahedral T_{1g} transition is shared between the trigonal A_2 and E_a transitions in the ratio $1 : \sqrt{2}$, it is required by eqns. (1) and (2) that the values of the electric moments of the A_2 and the E_a transitions stand in the ratio $\sqrt{2} : 1$. The intensity of the plane-polarised or unpolarised absorption is proportional to the dipole strength, which equals the square of the electric dipole transition moment, so that the absorption intensity of the A_2 transition would be twice that due to the E_a transition if the sum rule were exactly obeyed. The observed intensity ratios, $I(A_2)/I(E_a)$, are, however, less than 2 (Table 3), suggesting that the observed deviations from the sum rule (Table 1) are such that $R(E_a)$ has generally a larger magnitude than $R(A_2)$. Thus the signs of the major and the minor circular dichroism bands of a trigonal complex, in the region of the long-wavelength absorption, should give the signs of $R(E_a)$ and $R(A_2)$, respectively. The observation of only one circular dichroism band in that region, as in the case of (+)-Cr(en)$_3^{3+}$ and of (—)-Co(ox)$_3^{3-}$ (Table 1), signifies that $R(A_2)$ is completely overlapped and cancelled by the dominant $R(E_a)$, which is responsible for the residual circular dichroism measured in solution.

In general, the magnitude of the solution circular dichroism due to the E_a transition, identified by the first or the second method, is found to be larger than that of the circular dichroism due to the A_2 transition (Table 1), but there are two exceptions, (—)-Cr(mal)$_3^{3-}$ and (+)-Rh(—pn)$_3^{3-}$ (Figures 1 and 2), which indicate that the third method is not always reliable. The third method is dubious in the case of trigonal complexes where the influence of the trigonal field is small compared with that of the octahedral field, for the rotational strength of a transition depends upon the electric moment due to the trigonal field only, whereas the dipole strength of that transition is a sum of contributions from the trigonal and the octahedral field. Thus the dipole strength of the absorption due to the combined A_2 and E_a transitions for Cr(mal)$_3^{3-}$ and for Cr(ox)$_3^{3-}$ is, respectively, twice and seven times as large as that of the absorption due to the corresponding T_{1g} transition of Cr(H$_2$O)$_6^{3+}$. The measured intensity ratio, $I(A_2)/I(E_a)$ (Table 3), is thus a good approximation to the ratio of the corresponding trigonal dipole strengths for Cr(ox)$_3^{3-}$, but not for Cr(mal)$_3^{3-}$, where the trigonal and the octahedral contributions to the total dipole strength are probably similar in magnitude.

The configurations assigned to the trigonal complexes studied by means of the optical principle proposed above (Table 1) are in general accord with those related by Werner's solubility method [27] or Delepine's method [28] of active quasi-racemates. The $M(C_3)$ configuration is common to the isomers of the d^3 and d^6 ethylenediamine complexes forming the less-soluble halide-(+)-tartrate salt, and those of the corresponding malonate and oxalate complexes forming the less-soluble (—)-strychnine salt. In the latter series, the solubility criterion is not self-consistent, for either (+)- or (—)-Cr(ox)$_3^{3-}$ may be obtained as the less-soluble (—)-strychnine salt, depending upon the solvent.[29,30]

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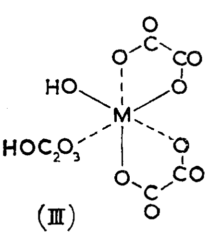
[27] A. Werner, *Ber.*, 1912, **45**, 1229.

[28] M. Delepine, *Bull. Soc. chim. France*, 1934, (5) **1**, 1256.

[29] A. Werner, *Ber.*, 1912, **45**, 3061.

[30] C. H. Johnson and A. Mead, *Trans. Faraday Soc.*, 1935, **31**, 1621.



(III)

The majority of the circular dichroism spectra reported are in accord with a trigonal structure for the complex studied, each spectrum consisting in general of the two circular dichroism bands due to the A_2 and the E_a transitions, followed at shorter wavelengths by a single circular dichroism band due to the E_b transition. A notable exception is (—)-$Co(ox)_3^{3-}$, which gives, in the shorter-wavelength region, three circular dichroism bands in solution (Table 1), but only one in the crystal (Table 2). The crystal circular dichroism supports a trigonal structure for the complex in the solid state, but the solution circular dichroism suggests that, in water, the complex has a lower symmetry, the three bands arising possibly from the B and the two A transitions into which the octahedral T_{2g} transitions breaks down in a complex with a structure belonging to the group C_2. Such a structure (III), in which one of the chelate rings has opened to give a free carboxylic acid group, has been suggested [4] from the circular dichroism evidence, but the acid–base titration curve shows [31] that $K_3Co(ox)_3$ has no acidic functional group with a pK_a value between 2 and 11.

Potentiometric titration of $K_3Rh(ox)_3$ in aqueous solution indicates similarly that this complex has no acidic functional group with an acid dissociation constant in the above range, although the proton magnetic resonance spectrum [32] of the salt in the solid state indicates that it consists of an equimolecular mixture of the tri-chelate and the bi-chelate complex (III). The circular dichroism spectrum of (+)-$Rh(ox)_3^{3-}$ in a uniaxial crystal is consistent with a trigonal structure for the complex-ion, however. At present, the detailed structure of these oxalate complexes remains uncertain.

EXPERIMENTAL

The optical isomers used were prepared by means of the methods described in the following references: (+)-Co(+pn)$_3$Cl$_3$,[13] [α] = +43°; (+)-Cr(en)$_3$I$_3$,[33] [α] = +60°; (—)-Rh(en)$_3$Cl$_3$,[34] [α] = —79°; (—)-K$_3$Co(ox)$_3$,[35] [α] = —4020°; (+)-K$_3$Cr(ox)$_3$,[35] [α] = +1600°; (—)-K$_3$Cr(mal)$_3$,[36] [α] = —150°; (+)-K$_3$Rh(ox)$_3$,[35] [α] = +82°; (+)-Co(+hmc)$_3$,[37] [α] = +335°; (+)-Cr(+hmc)$_3$,[37] [α] = +2000°. (—)-Propylenediamine complexes were obtained by the methods described [33,34] for the corresponding ethylenediamine complexes: (—)-Cr(—pn)$_3$Cl$_3$, [α] = —39°; (+)-Rh(—pn)$_3$Cl$_3$ [α] = +154°. The sign of the optical rotation specifying an isomer, and the specific rotations recorded, refer to the wavelength 5890 Å.

Hexagonal crystals of NaMgAl(ox)$_3$,9H$_2$O, containing (—)-$Co(ox)_3^{3-}$, (+)-$Cr(ox)_3^{3-}$, or (+)-$Rh(ox)_3^{3-}$, were grown by immersing thin plates of the host crystal, cut perpendicular to the optic axis, in a saturated solution of sodium magnesium aluminium oxalate containing the appropriate optical isomer. Crystals containing (—)-$Co(ox)_3^{3-}$ or, more particularly, (+)-$Cr(ox)_3^{3-}$ were grown at 0° in order to minimise the degree of racemisation. A growth period of 2—4 hr. gave crystals containing sufficient of the isomer for circular dichroism or optical rotatory dispersion measurements, which were made with the radiation propagated perpendicular to the (0001) face of the hexagonal plate. The concentration and the degree of optical purity of the isomer in the host crystal were determined by dissolving the crystal in water, and measuring the optical density of the solution at the wavelength of maximum absorption of the isomer in the visible region, and the optical rotation of the solution at 5890 Å. The axial circular dichroism of the hexagonal crystal, (—)-Rh(en)$_3$Cl$_3$,H$_2$O, was measured by the method described [22] for the corresponding cobalt(III) crystal.

Circular dichroism spectra were measured with a Jouan Dichrograph and with a circular dichroism spectrophotometer previously described.[38] Optical rotatory dispersion curves were measured with a Bellingham and Stanley spectrophotolarimeter, and were found, by means of

[31] C. Schäffer, personal communication.
[32] A. L. Porte, H. S. Gutowsky, and G. M. Harris, *J. Chem. Phys.*, 1961, **34**, 66.
[33] A. Werner, *Ber.*, 1912, **45**, 865.
[34] A. Werner, *Ber.*, 1912, **45**, 1228.
[35] F. P. Dwyer and A. M. Sargeson, *J. Phys. Chem.*, 1956, **60**, 1331.
[36] F. M. Jaeger, *Rec. Trav. chim.*, 1919, **38**, 171.
[37] I. Lifschitz, *Z. phys. Chem.*, 1923, **105**, 27.
[38] S. F. Mason, *J.*, 1962, 3285.

the dispersion–absorption relationships,[39] to agree with the circular dichroism curves. The absorption spectra were obtained with a Hilger Uvispek silica-prism spectrophotometer and an Optica double-beam grating instrument. 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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CHEMISTRY DEPARTMENT, UNIVERSITY OF EXETER.
[Present addresses: (R. E. B. and S. F. M.) SCHOOL OF CHEMICAL SCIENCES,
UNIVERSITY OF EAST ANGLIA, NORWICH.
(A. J. M.) CHEMISTRY DEPARTMENT IV,
UNIVERSITY OF COPENHAGEN.]
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[39] W. Kuhn, *Ann. Rev. Phys. Chem.*, 1958, **9**, 417.
[40] F. P. Dwyer and A. M. Sargeson, *J. Amer. Chem. Soc.*, 1959, **81**, 2335.