Optically Active Co-ordination Compounds. Part XXXVIII.[1] Circular Dichroism of Labile Trioxalatometallate(III) Complexes

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From solutions of kinetically labile or inert racemic complexes of the type $[M(C_2O_4)_3]^{3-}$ (M = V, Cr, Mn, Fe, or Co), addition of the resolving ions Λ- or Δ-$[M'(en)_3]^{3+}$ (M′ = Co or Rh; en = ethylenediamine) causes precipitation of diastereoisomeric salts $[M'(en)_3][M(C_2O_4)_3]\cdot xH_2O$. All the salts except that of Fe^{III} show circular dichroism in the visible region when measured as dispersions in CsCl discs. All the salts are isomorphous, so that stereochemical correlations are possible, using the rule of less-soluble diastereoisomers. Absolute configurations are assigned to the trioxalato-species. The circular dichroism spectra also confirm the Λ configuration of $(-)[Rh(en)_3]^{3+}$.

CHIROPTICAL spectroscopy is a useful stereochemical method of analysis, which is usually applied in solution or liquid phases. Once this constraint as to phase is removed, Cotton effects may be observed in several ways which have not all been widely appreciated, although they yield novel information. Of the 32 point groups available for crystallization, 11 lack all reflection symmetry. In order to achieve a crystallization within one of these 11 enantiomorphous point groups, from an initially optically inactive solution of a particular chromophoric species, several routes are available. These include the following. (*i*) Spontaneous resolution, whereby (*a*) a symmetric solution or melt gives crystals having an enantiomorphic space group rather than the reflectional symmetry expected, *e.g.* quartz, $Na[ClO_3]$, or α-$[Ni(OH_2)_6][SO_4]$, or (*b*) a solution of a racemate gives optically active single crystals, *e.g.* $K[Co(edta)]\cdot 2H_2O$ or $[M(en)_2(C_2O_4)]Br$ (M = Rh or Co; edta = ethylenediaminetetra-acetato and en = ethylenediamine). (*ii*) crystallizing (after suitable additions) a substance which is necessarily optically active, usually through the dissymmetry of a counter ion,[2] *e.g.* $[Co(NH_3)_6][(+)bcs]_3$ (bcs = bromocamphorsulphonate). The hexa-amminecobalt(III) chromophore must exist within a dissymmetric matrix and is therefore optically active. This is similar to the induction of activity in a symmetric chromophore by dissolution in an optically active solvent, *e.g.* $[PtCl_4]^{2-}$ in L-butane-2,3-diol[3] or potassium metal in[4] anhydrous (−)-propane-1,2-diamine (pn). A special case of this type for metal ions would be the use of a dissymmetric organic ligand to render the lattice dissymmetric; any kinetically labile metal ion with an excess of (+)-1,2-diamine or (+)-β-diketonate will give necessarily optically active complexes, *e.g.* $[Ni\{(+)pn)\}_3]$. (*iii*) Co-crystallizing to make a so-called partial or quasi-racemate; in the work of Delepine, some mixed dissymmetric crystals of species such as $K_3(+)[Rh(C_2O_4)_3]$ with $K_3[Al(C_2O_4)_3]$ must contain resolved trioxalatoaluminate(III), although no measurement of the optical activity of this species has ever been successful.§ (*iv*) Stabilizing one enantiomer of a rapidly interconverting pair by diastereoisomeric salt formation with a kinetically inert resolving agent. In

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§ The report by Burrows and Lauder[5] that a classical resolution of $[Al(C_2O_4)_3]^{3-}$ had been achieved using natural strychnine was later refuted.[6] However, Dwyer and Sargeson[6] did suggest, because of the similar stoicheiometries of the diastereoisomer $K[Ni(phen)_3][Co(C_2O_4)_3]\cdot xH_2O$ and the precipitate containing $[Al(C_2O_4)_3]^{3-}$, that the aluminate was presumably also resolved (phen = 1,10-phenanthroline).

[1] Part XXXVII, L. S. Dollimore and R. D. Gillard, *J.C.S. Dalton*, 1975, 369; a preliminary account of the present work was given at the Euchem conference on Optical Activity, Caen, France, May 1973 and by R. D. Gillard and D. A. Tarr, *Inorg. Chim. Acta*, 1975, **12**, L32.

[2] B. Bosnich and J. MacB. Harrowfield, *J. Amer. Chem. Soc.*, 1971, **93**, 4086.

[3] B. Bosnich, *J. Amer. Chem. Soc.*, 1967, **89**, 6143.

[4] P. V. Dowley, R. D. Gillard, P. R. Mitchell, and M. G. Price, *J. Chem. Soc.* (*A*), 1968, 2502.

[5] G. J. Burrows and K. H. Lauder, *J. Amer. Chem. Soc.*, 1931, **53**, 3600.

[6] F. P. Dwyer and A. M. Sargeson, *J. Phys. Chem.*, 1956, **60**, 1331.

the solid state the labile species is resolved; in solution, of course, it racemizes rapidly. Our recent resolution [7] of tricarbonatocobaltate(III) using (+)-tris(ethylenediamine)cobalt(III) was of this type.

The use of resolving agents which are similar in size to and of equal but opposite charge from the species to be resolved has been reviewed [8] and examples of the use of 3+ and 3− complex ions have been published.[9,10] We have now extended the method of isolating one enantiomer of a kinetically labile species by resolving trioxalatometallates(III) with the kinetically inert resolving agents $(+)[Co(en)_3]^{3+}$ and $(-)[Rh(en)_3]^{3+}$.

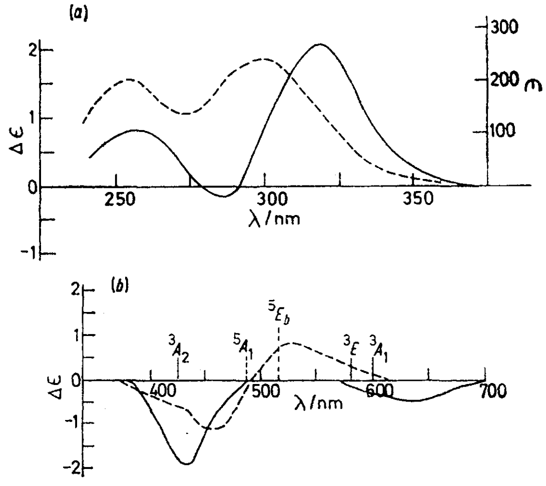
The relations between absolute configuration, absorption spectra, and circular dichroism have been much studied.[11] More recently, *X*-ray crystallography has provided [12] confirmation and correction of the configurational assignments of several complex ions. In spite of the many efforts, obtaining chiroptical spectra for labile complexes remained a problem until the recent use of dispersions in potassium halide discs.[13,14] This technique in principle allows measurements of spectra for any compound which does not racemize rapidly in the solid state. By combining $\Lambda(+)[Co(en)_3]^{3+}$ and $\Delta(+)$- or $\Lambda(-)$-$[Rh(en)_3]^{3+}$ as counter ions with dispersions in alkali-metal halide discs, notably caesium chloride, we have obtained circular-dichroism (c.d.) spectra for the labile ions $[V(C_2O_4)_3]^{3-}$ and $[Mn(C_2O_4)_3]^{3-}$. The absolute configurations have been related to the known structures of $\Lambda(+)[Cr(C_2O_4)_3]$ and $\Lambda(-)[Co(C_2O_4)_3]$ by *X*-ray powder photographs for the insoluble diastereoisomeric salts, and the absorption spectra and c.d. spectra have been correlated.

EXPERIMENTAL

Circular-dichroism spectra were measured with a model B Roussel–Jouan Dichrographe. Carbon, H, and N analyses were by Mr. G. H. J. Powell, using a Hewlett–Packard model 185 C, H, N analyser. $\Lambda(+)$-Tris(ethylenediamine)-cobalt(III) chloride [15] and $\Delta(+)$- and $\Lambda(-)$-tris(ethylenediamine)rhodium(III) chloride [16] were prepared by published procedures. Absorption and c.d. spectra agreed with the literature values to within 2%. The potassium trioxalatometallates(III) were prepared by standard methods (Fe,[17] Co,[17] Cr,[17] Mn,[18] and V[19]), as was sodium tricarbonatocobaltate(III)–water (1/3).[20]

General Procedure for Resolutions.—Approximately 100 mg of $K_3[M(C_2O_4)_3]\cdot 3H_2O$ and 50 mg of $\Lambda(+)[Co(en)_3]Cl_3\cdot H_2O$, $\Lambda(-)[Rh(en)_3]Cl_3\cdot 3H_2O$, or $\Delta(+)[Rh(en)_3]Cl_3\cdot 3H_2O$ were dissolved separately, each in 3 cm³ of water. When the two solutions were mixed, a fine precipitate formed almost immediately. This precipitate, removed from the solution by filtration or centrifuging, was washed at least three times with water (5 cm³), twice with absolute ethanol, and dried in air. Measurements were made on the resulting complexes as 1% dispersions in oven-dried KBr, KCl, or CsCl. The discs, of 13-mm diameter made in a standard disc press, usually contained 100 mg of the mixture. As checks on the procedure, $K_3\Delta(-)[Cr(C_2O_4)_3]$ and $K_3\Delta(+)$-$[Co(C_2O_4)_3]$ were precipitated from the filtrates of the preparations above by addition of acetone. No attempt was made to determine the optical purity of the resulting solid, but solution and disc c.d. spectra were recorded. The solution spectra agreed qualitatively with literature values, and the disc spectra prompted our choice of CsCl as the matrix for further c.d. spectra (see discussion below).

Spectra were recorded for the wavelength range 400—700 nm for all the discs, and extended to lower wavelengths when allowed by the quality of the disc. Scattering was severe below 400 nm, and even at high sensitivity the slit width was large. However, it is worth remarking that ultraviolet spectra in KCl discs have been measured [21] for wavelengths as low as 238 nm, so that solid-state circular dichroism may be useful for some organic chromophores. *X*-Ray powder photographs were obtained with a Siemens Kristalloflex 2 H apparatus equipped with a smoothing unit. A 1-rad camera and zirconium-filtered Mo-K_α radiation were used.



(*a*) Circular-dichroism (——) and isotropic-absorption spectra (- - - -) of $\Lambda(-)[Rh(en)_3]Cl_3\cdot 3H_2O$ in aqueous solution. The ordinate is quantitative. (*b*) Typical c.d. spectra of discs in caesium chloride: (——) $\Lambda(-)[Rh(en)_3]\Lambda[V(C_2O_4)_3]$; (- - - -), $\Lambda(-)[Rh(en)_3]\Lambda[Mn(C_2O_4)_3]$. The units of the ordinate here are dm³ mol⁻¹ cm⁻¹, as discussed in the text. The vertical lines marking transitions [(——), V ($^3A_2$ ground state); (- - - -), Mn (^5E_a ground state)] are those given in ref. 40

RESULTS

Using the ion $\Lambda(+)[Co(en)_3]^{3+}$, we isolated diastereoisomeric salts with the trioxalato-complexes of V^{III}, Cr^{III}, Mn^{III}, Fe^{III}, and Co^{III}. The c.d. spectra obtained for the

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[7] R. D. Gillard, P. R. Mitchell, and M. G. Price, *J.C.S. Dalton*, 1972, 1211.

[8] F. Basolo, *Co-ordination Chem. Rev.*, 1968, **3**, 213.

[9] J. W. Vaughn, V. E. Magnuson, and G. J. Seiler, *Inorg. Chem.*, 1969, **8**, 2101.

[10] L. S. Dollimore and R. D. Gillard, *J.C.S. Dalton*, 1973, 933.

[11] A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, 1965, 2883.

[12] K. R. Butler and M. R. Snow, (a) *J. Chem. Soc.* (*A*), 1971, 565; (b) *Chem. Comm.*, 1971, 550.

[13] R. D. Gillard and S. H. Laurie, *J. Chem. Soc.* (*A*), 1970, 59; *Chem. Comm.*, 1969, 489.

[14] B. Bosnich and J. MacB. Harrowfield, *J. Amer. Chem. Soc.*, 1972, **94**, 3425.

[15] J. A. Broomhead, F. P. Dwyer, and J. W. Hogarth, *Inorg. Synth.*, 1960, **6**, 183.

[16] F. Galsbøl, *Inorg. Synth.*, 1970, **12**, 269.

[17] J. C. Bailar and E. M. Jones, *Inorg. Synth.*, 1939, **1**, 35.

[18] G. H. Cartledge and S. P. Ericks, *J. Amer. Chem. Soc.*, 1936, **58**, 2061.

[19] A. Piccini and N. Briggi, *Z. anorg. Chem.*, 1899, **19**, 394.

[20] H. F. Bauer and W. C. Drinkard, *Inorg. Synth.*, 1962, **8**, 202.

[21] I. R. Beattie and M. Webster, *J. Phys. Chem.*, 1962, **66**, 115.

complexes $\Lambda(+)[Co(en)_3][M(C_2O_4)_3]$ in KBr discs showed the expected peaks of the $\Lambda(+)[Co(en)_3]^{3+}$ ion as well as additional shoulders and broadenings which can be attributed to the anions. By using the $\Lambda(-)[Rh(en)_3]^{3+}$ cation, whose absorption and circular dichroism in the visible region of the spectrum are negligible, the visible spectra of the oxalate complexes can be seen without interference. The spectra obtained from the rhodium salts are shown in the Figure and Table 3. All $\Delta\varepsilon$ ($= \varepsilon_l - \varepsilon_r$) values were calculated from the molar concentrations in the discs. However, since discs frequently give lower intensities than solution spectra and the intensities vary with the individual discs, these are useful mainly for qualitative comparisons. The results reported were all obtained from CsCl discs.

TABLE 1

Analyses (%) of $(-)[Rh(en)_3][M(C_2O_4)_3]\cdot xH_2O$

		Found			Calc.			
		C	H	N	C	H	N	x
V	*a*	23.7	4.4	13.8	23.7	4.2	13.8	0.5
	b	24.1	4.1	13.9	24.1	4.0	14.1	0
Cr	*a*	23.7	4.1	13.8	23.7	4.1	13.8	0.5
	b	23.8	4.0	13.8	24.1	4.0	14.0	0
Mn	*a*	23.3	4.3	13.3	23.2	4.2	13.6	1
	b	23.5	4.2	13.3	23.6	4.1	13.8	0.5
					23.9	4.0	14.0	0
Fe	*a*	23.3	4.3	13.5	23.2	4.2	13.5	1
	b	23.4	4.1	13.6	23.5	4.1	13.7	0.5
					23.9	4.0	13.9	0
Co	*a*	23.7	3.8	13.6	23.1	4.2	13.5	1
	b	23.5	4.1	13.7	23.4	4.1	13.7	0.5
					23.8	4.0	13.9	0

[a] Dried in air. [b] Dried *in vacuo* over $CaCl_2$.

TABLE 2

Sign of the longest-wavelength c.d. band in $[M(C_2O_4)]^{3-}$ in the insoluble diastereoisomeric salts

M	$\Lambda[Co(en)_3]\Lambda[M(C_2O_4)_3]$	$\Lambda[Rh(en)_3]\Lambda[M(C_2O_4)_3]$
V	−	−
Cr	−	−
Mn	+	+
Fe	*	*
Co	+	+

* The intensity of the visible spectrum of $[Fe(C_2O_4)_3]^{3-}$ is so low that no c.d. spectrum was observed in our solids, although a weak Cotton effect for this species in solution (induced by the Pfeiffer effect of natural cinchonine) was recently found at *ca.* 610 nm (N. Ahmad and S. Kirschner, *Inorg. Chim. Acta*, **1975**, **14**, 215).

TABLE 3

Circular-dichroism and absorption spectra of $\Lambda[M(C_2O_4)_3]^{3-}$

Ground state	Solids					Solutions [c]			
	C.d.[a]		Absorption [b]			Absorption		C.d.	
	λ/nm	Δε	λ/nm	D_3	O_h	λ	ε	λ	Δε
V $^3A_2$	630	−0.46	600 (π)	$^3A_1$					
			580 (σ)	^3E_b	$^3T_2$	605		600	+182
	430	−1.94	488 (π)	$^1A_1$					
			420 (π)	$^3A_2$		444		440	−786
$(+)_{589}$Cr $^4A_2$			691	^2E					
			655	$^2T_1$					
	610	−1.80	578 (π)	$^4A_1$	$^4T_2$	571	74	630	−0.58
	540	+2.02	568 (σ)	^4E_a				552	+2.83
			480						
	420	−0.82	422 (σ)	^4E_b	$^4T_2$				
				$^4A_{2b}$	$^4T_1$	422	97	415	−0.56
Mn ^5E_a	525	+0.92	498 [d]		$^5T_2$				
	455	−1.14							
$(-)_{589}$Co $^1A_1$	605	+1.16	612	^1E_a					
			606	$^1A_2$	$^1T_1$	602	153	617	+3.30
	420	−0.60	427	^1E_b	$^1T_2$	422	204	446	+0.26
	370	+0.34		$^1A_{1b}$				412	−0.26
								370	+0.21

[a] This work. [b] Oriented single-crystal data from ref. 40. [c] Data ($\Delta\varepsilon$/dm^3 mol^{-1} cm^{-1}) for Cr and Co from ref. 11; the data given for V are from Pfeiffer-effect studies in W. Ahmad and S. Kirchner, *Inorg. Chim. Acta*, 1975, **14**, 215; the Δε units are those of this reference. [d] The salt $[Mn(C_2O_4)_3]^{3-}$ gave a broad asymmetric band at 508 nm in a C_4Cl_6 mull, and, from reflectance spectra, assignments as λ 1098vb ($^5A_{1g}$) 525 ($^5B_{2g}$), 490 (^5E_g), and 339 nm ($^5A_{1g}$) from a split ^5E_g ground state (T. S. Davis, J. P. Fackler, and M. J. Weeks, *Inorg. Chem.*, 1968, **7**, 1994).

The absolute configuration of the $(+)[Co(en)_3]^{3+}$ ion has been established [22] as Λ [23] (earlier called [22] the D form). The $(-)[Rh(en)_3]^{3+}$ ion has also been assigned the Λ configuration on the basis [11] of circular dichroism. The solid-state c.d. spectra of the trioxalatometallates(III) confirm the identity of the two configurations. Two such similar ions with the same absolute configurations should precipitate with the same anion configuration, as is shown by Table 2. This argument was used [12b] by Butler and Snow when, having found $K(+)[Ni(phen)_3](-)_{589}[Co(C_2O_4)_3]\cdot 2H_2O$ to be isomorphous with $K(+)[Ni(phen)_3](+)[Cr(C_2O_4)_3]\cdot 2H_2O$, they then assigned the (+)-trioxalatochromate(III) the same Λ configuration as that known for $(-)_{589}[Co(C_2O_4)_3]^{3-}$.

X-Ray powder photographs show that the complexes $(-)[Rh(en)_3][M(C_2O_4)_3]\cdot xH_2O$ (M = V, Cr, Mn, Fe, or Co) are all isomorphous. The $(-)[Co(C_2O_4)_3]^{3-}$ ion has been

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[22] Y. Saito, K. Nakatsu, M. Shiro, and H. Kuroya, *Acta Cryst.*, **1955**, **8**, 729.

[23] Commission on Nomenclature of Inorganic Chemistry of the I.U.P.A.C., *Inorg. Chem.*, 1970, **9**, 1.

studied by single-crystal methods [12a] and related to (+)-$[Cr(C_2O_4)_3]^{3-}$ by powder photographs.[12b] The enantiomers precipitated here are both Λ. Therefore, the complexes of V, Mn, and Fe also have the Λ configuration. In this case, the more exact form [24] of the rule of less-soluble diastereoisomers predicts this result. When the same resolving ion is used to precipitate isomorphous less-soluble diastereoisomeric salts differing only in the central metal atom, the salts should have the same absolute configuration. This is a thermodynamic argument based on lattice-packing considerations. In some instances, nucleation and crystallization kinetics may override the thermodynamic factors. Sargeson obtained [25] only inactive precipitates with $\Lambda(+)[Co(en)_3]^{3+}$ and $[Co(C_2O_4)_3]^{3-}$, while Vaughn *et al.*[9] found active precipitates. We have observed both phenomena several times with $\Lambda(-)[Rh(en)_3]^{3+}$ and $[Co(C_2O_4)_3]^{3-}$, although temperature variations (as yet not studied) may also underlie this phenomenon.

Attempts to prepare the diastereoisomeric complex $\Delta(-)$-$[Rh(en)_3][Co(CO_3)_3]$ were unsuccessful. The precipitate formed was gelatinous and, even though an excess of Na_3-$[Co(CO_3)_3]$ was present in the original solution, the resulting filtrate was colourless. No c.d. spectrum was observed using CsCl discs containing the precipitate. In a similar way, Weick in these laboratories obtained [26] precipitation but no resolution with the system $(-)[Pt(en)_3]^{4+}$ and Durrant's salt (although it is not of course yet known whether this contains a DL or a *meso*-system).

DISCUSSION

Although recent studies [27] have cast some doubt on the comparison of c.d. spectra in solution and in alkali-halide dispersions, we find that for the diastereoisomers containing Cr and Co, where racemization is slow enough for measurements of optical activity in solution, the chiroptical properties in CsCl discs and in aqueous solutions are nearly identical. On the other hand, measurements in KBr and KCl discs were quite different. The spectrum of $\Lambda(-)[Rh(en)_3]$ $\Lambda(-)[Co(C_2O_4)_3]$ in KBr showed three peaks, positive at 610 nm and negative at 555 and 420 nm, of relative intensities $1 : -3 : -1.5$ respectively. In contrast, the solution spectrum of $\Lambda(-)[Co(C_2O_4)_3]^{3-}$ has [11] peaks at 617, 446, 412, and 377 of intensities $2 : 1 : -1 : 1$. The solution spectrum of $\Delta(+)$[Co-$(C_2O_4)_3]^{3-}$ from the supernatant was enantiomeric with the published spectrum of $\Lambda(-)[Co(C_2O_4)_3]^{3-}$ described above, but solid $K_3\Delta(+)[Co(C_2O_4)_3]$ isolated from this supernatant and measured in a KBr disc showed only peaks at 605 and 415 nm of intensities $-5 : 1$. In a KCl disc the peaks were similar, but the baseline changed dramatically between the two peaks (about half the height of the 605 nm peak). When CsCl was used as the matrix,[28] all the solution peaks appeared (605, 448, 410, and 370 nm, with intensities $-10 : -1 : 1 : -2$). The complex ions did not change in any permanent way in the different discs, since we find that the KBr and KCl discs dissolved in water to give solution spectra identical to that of the original complex. In the other cases examined there was no significant difference between KBr and CsCl discs.

The solid-state effects may arise in a number of ways. In this context, the variability between solution and disc c.d. spectra of the Λ β isomers of $[ML_3]$ (M = Co, Cr, or Rh; L = amino acid anion) has recently been discussed [29] in detail. Most obvious (although unlikely in view of the recovery of the original circular dichroism on dissolution) is a difference in the chemical nature of the species involved. Previous studies [30,31] have suggested that, in certain trioxalato-species, one oxalate ligand may be directly attached to the metal ion at one end only, with the other end being hydrogen bonded to a water molecule which in turn is bonded to the metal. The solution c.d. spectrum of $(-)[Co(C_2O_4)_3]^{3-}$ has been explained [11,32] as a result of a mixture of this species with the tris(bidentate) ion. Since the spectra in the CsCl disc and solution match, it is unlikely that the solid and solution species differ in this way. Recent crystal-structure studies have shown [12a,33] only tris(bidentate oxalate) ions even when attempts were made to fit the data with lower symmetries in the case of $K_3[Rh(C_2O_4)_3]\cdot4.5H_2O$. Another possibility which seems even less likely is halide displacement of one end of an oxalate. If this happened, the dissolved discs would have different spectra.

A more probable explanation is the presence of some special structural feature in the solid state which changes the local chiroptical field of the anionic tris(chelate). Although, from the work of Barron,[34] it is clear that quadrupolar effects do not contribute to the c.d. spectra of isotropic samples, other possibilities which might contribute include simple crystal-packing distortions, ion pairing, or hydrogen bonding within the crystal, phase changes caused by grinding and pressing with alkali halides, and contributions from larger-scale dissymmetry in the crystal. The net effect of all but the last would be a reduction in the symmetry of the near-octahedral MO_6 unit. Certainly, these salts of $[M(C_2O_4)_3]^{3-}$ are prone to double-salt formation and cation-exchange effects.

Circular-dichroism and polarized-absorption spectra of oriented single crystals of $\Lambda(+)[Co(en)_3]^{3+}$ have been measured and analyzed by using trigonal [35] and octahedral [36] approaches, and the question of effects of site

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[24] K. Garbett and R. D. Gillard, *J. Chem. Soc.* (*A*), 1966, 802.

[25] A. M. Sargeson in 'Chelating Agents and Metal Chelates,' eds. F. P. Dwyer and D. P. Mellor, Academic Press, New York, **1964**, p. 194.

[26] C. F. Weick, unpublished work, 1972.

[27] B. Bosnich and J. MacB. Harrowfield, *Inorg. Chem.*, 1975, **14**, 828.

[28] W. E. Hatfield, R. C. Fay, C. E. Pfluger, and T. S. Piper, *J. Amer. Chem. Soc.*, 1963, **85**, 265.

[29] R. D. Gillard, S. H. Laurie, D. C. Phillips, D. A. Phipps, and C. F. Weick, *J.C.S. Dalton*, 1974, 1385.

[30] R. D. Gillard, S. H. Laurie, and P. R. Mitchell, *J. Chem. Soc.* (*A*), 1969, 3006.

[31] A. L. Porte, H. S. Gutowsky, and G. M. Harris, *J. Chem. Phys.*, 1961, **34**, 66.

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

[33] B. Dalgell and K. Eriks, *J. Amer. Chem. Soc.*, 1971, **93**, 4298.

[34] L. D. Barron, *Mol. Phys.*, 1972, **23**, 1027.

[35] (*a*) A. J. McCaffery and S. F. Mason, *Mol. Phys.*, 1963, **16**, 359; (*b*) A. J. McCaffery, S. F. Mason, and B. J. Norman, *Chem. Comm.*, 1966, 661.

[36] R. Dingle and C. J. Ballhausen, *Kgl. Dansk. Vidensk. Sel. Mat. Fys. Medd.*, 1967, **35**, 1.

symmetry on the observed c.d. spectra has been investigated [35b] using different salts in KCl and KBr discs and in aqueous solution. Chloride, bromide, and perchlorate ions and digonal and trigonal symmetries have only minor effects on the c.d. spectra. The crystal structures [37] of trioxalato-salts (usually with small cations like potassium) show symmetries lower than octahedral for the MO_6 unit (OMO angles differ by as much as 14°).

There are plenty of cases [38,39] in which ion pairing changes the optical rotatory dispersion (o.r.d.) or c.d. spectrum of an active ion in aqueous solution. Although the effects of changing anions on the c.d. spectra in the solid state of $\Lambda(+)[Co(en)_3]^{3+}$ were rather small, the exchange of ions differing in size as much as K^+ and Cs^+ could be significant in altering the spectra of the trioxalato-anions. More specific interaction between the $\Lambda(-)[Rh(en)_3]^{3+}$ and $\Lambda(-)[Co(C_2O_4)_3]^{3-}$ ions seems likely. The difference between $K_3\Delta(+)[Co(C_2O_4)_3]$ and $\Lambda(-)[Rh(en)_3]\Lambda(-)[Co(C_2O_4)_3]$, each in CsCl, is similar to that between CsCl and KBr discs of $K_3\Delta(+)[Co(C_2O_4)_3]$. For our present purpose, the comparison of isomorphous salts of the series $\Lambda(-)[Rh(en)_3][M(C_2O_4)_3]$, it seems probable that any specific local influence within one lattice will recur throughout the series. The similarity of the spectra in solution and CsCl disc of $K_3\Delta(+)[Co(C_2O_4)_3]$ suggests that no major changes take place in the CsCl matrix.

Theories of the optical activity in the *d–d* region of trigonal compounds belonging to the D_3 point group (with symmetrical ligands such as ethylenediamine, oxalate, malonate, pentane-2,4-dione, 2,2′-bipyridine, or 1,10-phenanthroline) or to the C_3 point group (with unsymmetrical ligands such as amino acids, propylenediamine, or 5-nitro-1,10-phenanthroline) rest on the notion that there is trigonal splitting of the T excited states into E and A states. The observed circular dichroism in the region of band (1) then arises from the transitions (of opposite rotational strengths) from the ground state to the A and E levels.

An alternative view is that Jahn–Teller splitting of the states is at least as important. This has been suggested several times but has not been fully developed. We cannot, at present, completely account for the spectra we have observed and the different effects of the salt matrices used. The discussion below of the results in Table **3** is necessarily rather tentative and qualitative.

Chromium.—The spectrum of $K_3(-)[Cr(C_2O_4)_3]$ in CsCl is nearly identical to the aqueous solution spectrum with only minor changes in intensity. However, the spectrum of $\Lambda(-)[Rh(en)_3]\Lambda(+)[Cr(C_2O_4)_3]$ in CsCl shows more marked differences in wavelength and intensity. The longest-wavelength peak has moved from 630 to 610 nm, the middle peak from 552 to 540 nm, and the intensities are nearly equal, in contrast with the 1 : 5 ratio of the solution measurements. The peak at 420 nm is also relatively more intense than in solution. The change from solution to solid in the intensity ratios of the components under band (1) (*i.e.* at 610 and 540 nm) is strongly reminiscent of the similar changes for the tris(amino-acid anion) complexes of Cr^{III} and Co^{III} which were noted [29] recently. In that case, the solid spectra were obtained in Nujol mulls as well as KBr discs. A common feature in the two cases β-$[ML_3]$ and $[M'(en)_3]$-$[M(C_2O_4)_3]$ is the possibility of hydrogen-bonding parallel to the three-fold molecular axis. This seems a likely feature in the crystal structure of $\Lambda[M'(en)_3]\Lambda[M(C_2O_4)_3]$, with the simplest possibility that the C_3 axes of both ions are collinear, with a set of specific hydrogen bonds from the N–H groups of the cation to the free oxygen atoms of the oxalate ions in the anion. More complicated hydrogen-bonding schemes cannot be excluded.

Cobalt.—The complex $\Lambda(-)[Rh(en)_3]\Lambda(-)[Co(C_2O_4)_3]$ in CsCl shows two peaks near 400 nm where $K_3\Lambda(-)$-$[Co(C_2O_4)_3]$ in solution and in CsCl shows three. This could be explained if there are only two fundamental absorptions in this region whose wavelength and intensity are shifted by different crystal lattices. In this case, the spectra in solution and CsCl disc of $K_3\Delta(+)[Co(C_2O_4)_3]$ have a broad peak of the same sign as the 620 nm peak superimposed on a narrower peak of opposite sign. The result shows a little of the broad peak at each side and the narrower peak dominating the middle. In KCl or KBr, the central narrow band increases in intensity and dominates the spectrum. In oriented single crystals, the broader peak dominates and the overall intensity is ten-fold higher. Possible sources of this intensity were discussed above. In $\Lambda(-)[Rh(en)_3]\Lambda(-)[Co(C_2O_4)_3]$ the wavelengths shift enough to separate the two peaks.

Manganese.—In solution, $K_3[Mn(C_2O_4)_3]$ shows a broad absorption band covering 450—525 nm and a very intense band below 340 nm. In an oriented crystal, the band is centred at 500 nm, with the ^5E component at lower energy than the $^5A_1$. In the c.d. spectrum of $\Lambda(-)[Rh(en)_3][Mn(C_2O_4)_3]$ in CsCl the two bands are more widely separated and have opposite signs. Presumably the positive band is due to the ^5E_b transition, the negative to the $^5A_1$. It is, of course, in this high-spin d^4 system that we expect a massive splitting of the ground state through the operation of the Jahn–Teller effect. The isomorphism found for $[Rh(en)_3][Mn(C_2O_4)_3]$ with the series $[Rh(en)_3][M(C_2O_4)_3]$ containing spherically symmetric d shells for M = Cr, Fe, and Co suggests that, within the time scale of the X-ray determination, the manganese complex does not display steric distortion.

Vanadium.—The complex $K_3[V(C_2O_4)_3]$ in solution has an absorption band at 600 nm and a very intense band below 450 nm. The crystal spectrum is similar, with a spin-forbidden band at 488 nm. The c.d. spectrum of $\Lambda(-)[Rh(en)_3][V(C_2O_4)_3]$ shows negative peaks at 630 and 430 nm, corresponding to the allowed transitions. Whether this ion is sufficiently close to octahedral that the

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[37] Vanadium; R. H. Fenn, R. D. Gillard, and A. J. Graham, *Nature*, 1967, **213**, 1012; Chromium; J. N. van Niekerk and J. R. L. Schoening, *Acta Cryst.*, 1952, **5**, 196 and 499; Iron; P. Herpin, *Bull. Soc. franc. Min. Crist.*, 1958, **81**, 245; Iridium; *ibid.*, p. 201; Cobalt; ref. 12*a*; Rhodium, ref. 33.

[38] M. J. Albinak, D. C. Bhatnagar, S. Kirschner, and A. F. Sonnessa, *Canad. J. Chem.*, 1961, **39**, 2360.

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

E and A components are not split apart, or whether one is large enough to cancel the other, cannot be determined from the results. Piper and Carlin[40] assigned {in $[V(C_2O_4)_3]^{3-}$ in a host lattice} two bands at 580 and 600 nm to transitions from the $^3A_2$ ground state to the trigonal components of $^3T_{2g}(O_h)$, *i.e.* ^3E_b and $^3A_1$ respectively. This situation is very similar to that for d^3 and we should expect (on the basis that E and A have opposite rotational signs and that trigonal splitting for V is at least as big as for Cr^{III}) that c.d. bands of opposite signs would be observed in this region for $[V(C_2O_4)_3]^{3-}$ as they are for $[Cr(C_2O_4)_3]^{3-}$. This is not the case.

The single c.d. band observed is centred at 630 nm, nearer the π-polarized single-crystal absorption assigned to $^3A_1 \leftarrow {}^3A_2$. In the trigonal theory, within the Λ absolute configuration we expect positive Cotton effects for E transitions but negative ones for A transitions. In this respect, if we assign the observed c.d. band to the A transition, $[V(C_2O_4)_3]^{3-}$ could be made consistent with the other metallates. However, when only one c.d. band is observed under band (1) it is always assumed to arise from the E component. No case is known of a single c.d. band in this region arising from the rotational strength of A exceeding that of E. We could equally well assign the vanadium c.d. band to the Jahn–Teller component $^3A_2$.

The spectra of all the present trioxalato-species except $[V(C_2O_4)_3]^{3-}$ could be readily interpreted as supporting the use of the E component of the long-wavelength band for assigning absolute configuration. However, since Butler and Snow have shown[12b] that it does not fit the $[Cr(malonate)_3]^{3-}$ case, and $[V(C_2O_4)_3]^{3-}$ shows opposite sign for the long-wavelength band to the E components of the other ions studied here, it seems that this means of establishing absolute configuration is not always valid. Piper's approach[41] using distortions of the octahedron to determine signs of the circular dichroism seems more promising, as recently indicated by Strickland and Richardson,[42] but it requires accurate crystallographic data.

One final comment should be made on theories depending on trigonal splittings. The optically active series of complex anions $[CoL_3]^{3-}$ (L = CO_3, C_2O_4, or $OC{\cdot}CH_2{\cdot}CO_2$) is known. The c.d. maxima for these ions are all at *ca.* 620 nm. The trigonal distortion must surely be greatest for the species $[Co(CO_3)_3]^{3-}$ with the smallest chelate ring. {Although the detailed structure of this anion is not as yet known, the two known structures with carbonato-groups chelated to Co^{III}, *i.e.* $[Co(NH_3)_4(CO_3)]Br$[43] and $[Co(tn)_2(CO_3)][ClO_4]$[44] (tn = propane-1,3-diamine) have angles at cobalt of *ca.* 70°.} However, the observed c.d. spectrum of $[Co(CO_3)_3]^{3-}$ shows only one sign. Facts of this kind support the view that the optical activity of transition-metal complexes requires further elucidation, with particular attention to metals other than cobalt and chromium, and, in the present work, we have begun to acquire experimental results on the configurational optical activity of a series of analogous chelated complexes ranging across the first transition series. Obvious extensions to the present method of resolution are to other relatively labile triply charged anions such as trioxalatoruthenate(III) and we will report on some of this work elsewhere.

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[40] T. S. Piper and R. L. Carlin, *J. Chem. Phys.*, 1961, **35**, 1809.

[41] T. S. Piper and A. G. Karipides, *Mol. Phys.*, 1962, **5**, 475.

[42] R. W. Strickland and F. S. Richardson, *Inorg. Chem.*, 1973, **12**, 1025.

[43] G. A. Barclay and B. F. Hoskins, *J. Chem. Soc.*, 1962, 586; the findings were independently confirmed by C. O. Haagensen and S. E. Rasmussen, *Acta Chem. Scand.*, 1963, **17**, 1630.

[44] R. J. Geue and M. R. Snow, *J. Chem. Soc.* (*A*), 1971, 2981.