X-Ray Structure, Absolute Configuration, and Circular Dichroism Spectra of Cobalt and Chromium Malonate Complexes as their Diastereoisomers, $\Delta[Co\{(-)1,2\text{-diaminopropane}\}_3]\Lambda[M(malonate)_3],3H_2O$

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The complexes $K_3[M(malonate)_3]$ (M = Co or Cr) have been resolved *via* their diastereoisomers with $(-)_{589}$-$[Co\{(-)1,2\text{-diaminopropane}\}_3]Br_3$. The only diastereoisomers precipitated are shown to have the absolute configurations $\Delta[Co\{(-)1,2\text{-diaminopropane}\}_3]\Lambda[M(malonate)_3],3H_2O$ where M is $(+)_{589}$Cr or $(-)_{589}$Co. Crystals of the chromium diastereoisomer are rhombohedral, space group R_{32}, with hexagonal lattice parameters, $a = 16.12(2)$, $c = 10.07(2)$ Å, and $Z = 3$. The structure was solved by Patterson and Fourier methods, and refined by full-matrix least-squares calculations to R 0.073 for 435 independent reflexions collected photographically. Both complex ions are disordered on sites of symmetry 32, and are linked in columns by three N–H · · · O hydrogen bonds. The columns of complexes are connected by hydrogen bonds involving both anion and cation. The cation adopts the expected $\Delta(\lambda\lambda\lambda)$ conformation with the methyl groups equatorial on the gauche rings. The malonate chelate ring skeleton is planar except for the methylene carbon atom. The absolute configuration of the $(+)_{589}[Cr(malonate)]_3^{3-}$ ion is opposite to an earlier assignment based on spectroscopic data. The circular dichroism spectra of the diastereoisomers as KBr discs show one less peak than is observed in the solution spectra of both $\Delta[M(malonate)_3]^{3+}$ complexes in the region of their T_{1g} transitions. The remaining peak has the same sign for both cobalt and chromium complexes. In these spectra and in those of the diastereoisomers $\Lambda[M(oxalate)_3]$ $\Lambda[Co(ethylenediamine)_3]$ (M = Co or Cr), the region of the T_{1g} transition of the tris(diamine) cations resemble the c.d. spectra of these cations in solution with added phosphate ion. The structure of the tris(malonate) diastereoisomer shows a similar hydrogen bonding scheme to that of a phosphate salt of the cation. In these diastereoisomers the complex cations have a similar effect in influencing the transition moments of the oxalato- and malonato-complex anions and it is therefore not readily possible to interpret solid to solution spectral changes in stereochemical terms.

AT present the only definitive ways of assigning the absolute configurations of metal complexes are chemical relation to a compound of known chirality, *e.g.* complexes of (—)pn (pn is 1,2-diaminopropane) derivatives,[1-3] and *X*-ray structure solution employing the property of anomalous dispersion [4] or incorporating in the crystal a molecule or molecular fragment of known absolute configuration.[5] It is currently held that the absolute configurations of chiral chromophores should most readily correlate with the features of their circular dichroism (c.d.) spectra.[6,7]

Despite the fact that the Cotton effect was first observed for an inorganic system,[8] the development of widely applicable theoretical models lags behind the theoretical interpretation of the phenomenon in organic chemistry.[9] This is partly a consequence of the differences in the electronic transitions being studied, and in the inorganic sphere theory best describes the experimental facts for the $\pi \rightarrow \pi^*$ transitions of unsaturated ligands such as 1,10-phenanthroline and 2,2′-bipyridyl when chelated to transition-metal ions.[10,11] For transition-metal complexes containing saturated ligands such as the aliphatic diamines, the transitions most studied have been the low-intensity spin-allowed *d–d* transitions centred on the metal ion and generally observable in the visible spectral region.[12]

The precise details of the c.d. spectra of a transition-metal complex are related to its symmetry, the spectroscopic interpretation being least complex for ions of high symmetry. The highest symmetry transition-metal complexes capable of existing as enantiomers have trigonal-dihedral (D_3 or 32) symmetry *e.g.* $[Co(en)_3]^{3+}$, $[Co(ox)_3]_3^-$, and $[Ni(o\text{-phen})_3]^{2+}$ (en = ethylenediamine, ox = oxalate, *o*-phen = *o*-phenanthroline), and it is these which have been studied most extensively theoretically.[13] Aware of the importance of the structure and absolute configuration of trigonal complex ions to the empirical c.d. correlations, the *X*-ray structures of the latter two ions have been reported as their diastereoisomer [14] as well as the structures of $KCa(+)[Co(dithiooxalate)_3],4H_2O$ [15] and $(+)[Co(biguanide)_3]Cl_3,$-$H_2O$.[16] The ligands with oxygen donor atoms, with the exception of oxalate, have been relatively neglected till recently and it was thought that the six-membered chelate ring of malonate would provide a significant perturbation to the chromophore geometry. Absolute configurations of the complexes $(+)_{546}[Co(en)(mal)_2]$ and $(+)_{589}[Cr(mal)_3]$ had been assigned [12,17] from c.d. data,

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but no structural descriptions of co-ordinated malonate (mal) were available. Brief reports of the structures and absolute configurations of these complexes [18] and the resolution of $K_3[Co(mal)_3]$[19] have been published. The full details and interpretation are presented here.

EXPERIMENTAL

Preparation of $K_3[Cr(malonate)_3],3H_2O$.—The dichroic blue-green microcrystalline powder obtained by reduction of potassium dichromate [20,21] was similar (i.r. and visible spectra, analysis, *X*-ray powder patterns) to the product obtained by the method of Lapraik [22,23] starting with freshly prepared $Cr(OH)_3$. Elution of independently prepared K_3- and Na_3-$[Cr(mal)_3]$ samples from AG1 X4 anion exchange resin in the chloride form showed 3—5 bands for all preparations. No attempt was made to determine the nature of the species in the minor bands (probably bis- and mono-malonates [24]) since the major component always eluted last with aqueous chloride solution suggesting a predominance of the trivalent tris-chelate. An i.r. spectrum obtained from a KBr disc of one preparation was almost identical with the published spectrum [25] and as all preparations were subsequently shown to give identical crystalline precipitates with $(-)[Co\{(-)pn\}_3]^{3+}$ further characterisation was considered unnecessary.

Preparation of $K_3[Co(malonate)_3],4H_2O$.—This complex was prepared by the method of Kneten and Spees.[26] The emerald green needles of the racemate were characterised by determination of crystal data: $K_3[Co(C_3H_2O_4)_3],4H_2O$, $M = 547.5$, Orthorhombic, space group $Pna2_1$, $a = 21.32$, $b = 12.07$, $c = 14.05$ Å, $U = 3\,617$ Å^3, $D_m = 2.00_7$ g cm^{-3} (by flotation), $Z = 8$, $D_c = 2.01$. The solution absorption spectrum was identical with that reported.[26] Ion-exchange chromatography indicated the presence of two components, a narrow very faint green band moving even more slowly than the major green $[Co(mal)_3]^{3-}$ species. Aqueous solutions become pale pink when set aside and the rate of decolouration is accelerated by light; a similar but much slower colour change occurs in the solid state and probably indicates decomposition to Co^{II} malonate and bis(malonate) species analogous to the solid-state decomposition [27a] of $K_3[Co(ox)_3],3H_2O$ on prolonged exposure to sunlight.

Preparation of $\Lambda(+)[Co(en)_3][M(ox)_3]$, $M = (-)Co$ *and* $(+)Cr$.—The potassium oxalato-salts were prepared by standard methods [27b] and resolved by use of $(+)[Ni(o\text{-phen})_3]Cl_2$ [28] to give $K_3(-)[Co(ox)_3]$ and $K_3(+)[Cr(ox)_3]$. The diastereoisomers with previously resolved $(+)[Co(en)_3]^{3+}$ ion were precipitated from concentrated aqueous solution of equimolar amounts of the optically active complexes. This procedure was followed since it was reported [29a] that $(+)[Co(en)_3]Cl_3$ is an ineffective resolving agent for these oxalate complexes. Recently, however, successful resolutions have been reported with this complex.[29b]

Resolution of $K_3[M(malonate)_3],xH_2O$ ($M = Cr$, Co).—Partial resolution of $K_3[Cr(mal)_3]$ as the strychnine salt has been reported.[20] Attempted resolution of the complex by this method was unsuccessful: crystallization of the racemic salt proved difficult because of its extreme solubility and sensitivity to slight changes in pH. No precipitate could be obtained with the cations $(+)[Co(en)_3]^{3+}$, $(+)[Ni(o\text{-phen})_3]^{2+}$, and strychnine. The complex $(-)[Co\{(-)pn\}_3]^{3+}$, however, initiated instantaneous growth of fine needles from dilute solutions. These crystals had appreciable solubility only at low pH levels where racemisation and aquation occurred. Crystals suitable for *X*-ray work were prepared by layering a solution of *trans*-$(-)[Co\{(-)pn\}_3]Br_3$ (ref. 30) on a more concentrated solution of $K_3[Cr(mal)_3],3H_2O$. Well formed crystals of *trans*-$(-)[Co\{(-)pn\}_3](+)_{589}[Cr(mal)_3],3H_2O$ grew during several hours. The sign of optical rotation was deduced from that given by the remaining solution.

A solution of $K_3[Cr(malonate)_3],3H_2O$ (0.040 g) in water (1 ml) was treated dropwise with $(-)[Co\{(-)pn\}_3]Br_3$ (0.019 g) in water (1 ml) and set aside in an ice bath for 3 min. The filtrate was passed down a cation exchange resin (Dowex 50W/4, potassium form) and the chiro-optical properties were measured immediately. $\{[\alpha]_{589} -103°$ may be compared with a lit. value [12] based on a strychnine resolution,[20] $-150°.\}$ The molar c.d. $(\varepsilon_l - \varepsilon_r)$ obtained [620 nm (+0.12), 546-(−0.29), 415(+0.09), and 372(−0.04)] however, are larger than found in that study.[12] The complex was not crystallised to constant rotation owing to its extreme solubility in water, as well as the small scale of the preparation, and the possibility of decomposition reactions. No further precipitation from the solution could be obtained by adding excess of resolving agent which suggests that the resolution is quantitative (Found: C, 30.3; H, 5.7; N, 11.5. $C_{18}H_{42}CoCrN_6O_{15}$ requires C, 31.2; H, 6.1; N, 12.1%). The complex $K_3[Co(mal)_3],3H_2O$ was similarly resolved; its half-life for racemisation at room temperature in solution is *ca.* 4 h. The chiro-optical spectra of the solutions were all measured in the period from 30—90 min from resolution. The o.r.d. spectrum of the filtrate exhibits only a small positive value at 489 nm, at 600 nm a specific rotation, $[\alpha]^{25}_{600}$, of 384° was measured *ca.* 30 min after resolution. The molar c.d., $\varepsilon_l - \varepsilon_r$, are 661 nm (−0.95), 593 (+0.85), 460 (−0.027), 423 (+0.12), and 385 (− 0.13). *X*-Ray Debye–Scherer powder photographs showed the cobalt and chromium diastereoisomers to be closely isomorphous. The diastereoisomer in the case of the cobalt malonate is therefore *trans*-$(-)[Co\{(-)pn\}_3](-)_{600}[Co(mal)_3],3H_2O$.

Powder photographs of the diastereoisomers were recorded by use of nickel-filtered Cu-K_α radiation and a Nonius general purpose camera (r 28.65 mm). Background fogging due to fluorescent scatter from Co was reduced by placing a dummy film in front of the intensity recording film. The c.d. curves and o.r.d. measurements were obtained by use of a Cary model 60 spectropolarimeter. The KBr discs were prepared by pressing at 10 tons sq. in^{-1} with an aluminium foil gasket from 2% samples previously ground in a dental mill. Only thin transparent discs were accepted,

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their absorption spectra were not recorded and no attempt was made to obtain extinction coefficients for the c.d. spectra.

Crystal Data.—$C_{18}H_{42}CoCrN_6O_{15}$, $M = 693.6$, Trigonal, with hexagonal lattice parameters, $a = 16.12(2)$, $c = 10.07(2)$ Å, $U = 2\,265(7)$ Å^3, $D_m = 1.52(2)$ (by flotation), $Z = 3$, $D_c = 1.53$ g cm^{-3}, $F(000) = 1\,089$. Space group R_{32}, Mo-K_α filtered by Zr, $\lambda = 0.7107$ Å; μ(Mo-K_α) = 10.3 cm^{-1}.

Bronze prisms of *trans*-$(-)_{589}$[Co($-$)pn)$_3$]$(+)_{589}$[Cr(mal)$_3$],3H$_2$O were triangular in section and showed extinction parallel to the needle axis, but no extinction viewed down their cross-section. Preliminary Weissenberg and precession photographs of several crystals confirmed the trigonal system: indexing on hexagonal axes established the condition limiting observed reflections as $-h + k + l = 3n$. The full set of intensity photographs (Mo-K_α radiation, see later) have Laue symmetry $\bar{3}m$ (32 and centre) even for layers of the type $hkl_{(2n+1)}$ for which the metal-atom contributions virtually cancel. Corresponding Cu-K_α photographs show the expected loss of exact mirror symmetry caused by anomalous scattering by cobalt and confirm point-group 32. Intensity data were collected from a crystal of dimensions 0.40 mm long with triangular cross-section edges 0.15 mm and mounted parallel to c, the needle axis. The intensities on layers with $l = 2n + 1$ were much weaker than those of the even layers, a consequence of the Co and Cr atoms with similar scattering power being separated by $c/2$ in the unit cell. By use of Mo-K_α radiation (Zr filter) integrated triple-film packs were recorded for the equi-inclination Weissenberg layers hk0–8 and hk10. The layers h0—3l were recorded as integrated precession photographs from the same crystal without remounting. The integrated data were measured photometrically with a Nonius II microdensitometer. Interfilm and interlayer scale factors were determined by a weighted, non-iterative, least-squares algorithm as described previously.[14] The initial data set comprised 426 reflections of which 35 were unobservedly weak. A further 25 reflections (layer hk7), which could not be initially included as their scale factor was undetermined by the scaling procedure, were included later. Data were corrected for Lorentz and polarisation effects, but not for absorption; the variation in transmission factors for any layer was estimated at 2% or less.

TABLE 1

Positional ($\times 10^4$) and thermal ($\times 10^5$) parameters for ($-$) [Co{($-$)pn}$_3$](+)[Cr(mal)$_3$],3H$_2$O *, with estimated standard deviations in parentheses

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cation									
Co	0	0	0	248(26)	248	552(30)	124	0	0
N(1)	677(10)	1 145(7)	1 122(8)	254(77)	390(74)	784(87)	123(68)	−8(57)	9(47)
C(1)	1 677(10)	1 706(9)	735(11)	391(89)	309(79)	573(124)	−30(69)	−97(66)	−31(69)
C(2)	2 264(24)	2 689(22)	1 325(23)	630(228)	283(174)	1 290(270)	137(175)	−123(170)	21(137)
Anion									
Cr	0	0	0.5	277(29)	277	526(36)	139	0	0
O(1)	1 124(5)	564(10)	3 845(6)	226(54)	531(72)	777(73)	169(66)	115(38)	433(60)
C(3)	1 851(10)	463(11)	3 899(9)	425(94)	708(116)	279(102)	270(89)	92(65)	139(68)
C(4)	432(29)	2 205(21)	4 620(32)	1 622(462)	414(198)	1 726(528)	706(257)	−1 443(350)	−560(208)
O(2)	2 647(24)	1 022(22)	3 226(35)	212(168)	504(251)	1 189(289)	15(166)	−89(125)	488(197)
O(3)	2 391(33)	601(28)	3 001(34)	−598(244)	676(297)	1 130(316)	−259(219)	11(171)	255(234)
Water				B/Å^2					
O(4)	2 427(10)	0	0	4.74(27)					
Calculated H atom positions									
N(1)H(1)	378	1 534	1 020	4.0					
N(1)H(2)	631	966	2 026	4.0					
C(1)H(1)	1 949	2 393	1 040	4.0					
C(1)H(2)	2 040	1 411	1 142	4.0					

* The form of the anisotropic thermal elipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}hk + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Isotropic thermal parameters given for O(4) and hydrogen atoms. Atoms C(2), C(4), O(2), O(3), O(4), and C(1)H(1) had multipliers of 0.5.

Solution and Refinement of the Structure.—The space group R_{32} ($Z = 3$) requires that both Co and Cr ions occupy the special positions of 32 symmetry at (0,0,0) and (0,0,$\frac{1}{2}$). The initial Fourier map [31] phased on these atoms leads to a position for the donor atoms averaged by the false centre introduced at (0,0,$\frac{1}{4}$). Introduction of the ($-$)[Co{($-$)pn}$_3$] complex in its $\Delta(\lambda\lambda\lambda)$ configuration (less methyl groups) gave R 0.234 ($l = 2n$ 0.147, $l = 2n + 1$ 0.508). Two cycles of full-matrix least-squares refinement minimising $\Sigma w(|F_o| - |F_c|)^2$, where w are the reflection weights assigned during data reduction, gave R 0.209. A subsequent Fourier map suggested a Λ configuration for (+)[Cr(mal)$_3$]$^{3-}$, but the structure solution had to proceed atom-by-atom in successive Fourier maps. This necessity arose since the ions are on sites of 32 symmetry and it was essential to correctly unravel the nature of the anticipated disorder. Isotropic refinement of all non-hydrogen atoms of the partially disordered model obtained gave R 0.092 ($l = 2n$ 0.087, $l = 2n + 1$ 0.1521). Gross outliers in the data set were checked, the weighting scheme was adjusted during fresh data reduction, to give a flatter distribution of $w(|F_o| - |F_c|)^2$ averaged in ranges of $|F_o|$ *vs.* $|F_o|$ and the hk7 data were included in the data set to be refined with a separate scale factor. Refinement was continued with anisotropic temperature factors for non-hydrogen atoms, and hydrogen atoms not subject to disorder were included at their calculated positions with isotropic temperature factors, but were not refined. Imaginary scattering components, $\Delta f''$ for Co^{2+} (1.0) and Cr^{2+} (0.7) were included in the calculations.[31a] The agreement factors at convergence were R 0.073 ($l = 2n$ 0.064, $l = 2n + 1$ 0.121) and R' 0.083. Symmetry restrictions

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[31] (*a*) D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17; (*b*) 'International Tables for Crystallography,' vol. III, Kynoch Press, Birmingham, 1962, p. 202; (*c*) Programs used for the solution, refinement, and geometry calculations were local modifications of the following: W. R. Busing and H. A. Levy's ORFLS and ORFFE, Zalkin's FORDAP, C. Johnson's ORTEP, and J. F. Blount's PLANE and BLANDA.

were applied to the anisotropic temperature factors of the metal atoms, but the water molecule could not be refined satisfactorily with other than an isotropic parameter. The thermal parameters of O(3) remained non-positive definite and unrealistic. This problem arises from a disorder of the atom (see Discussion section) and also possibly from the high correlation of its parameters with those of O(2) to which it is related by an approximate non-crystallographic mirror plane coincident with the atoms Cr, O(1), and C(3). A final difference map revealed peaks 0.5 eÅ^{-3} in height on the *c* axis near to the metal atoms. The chelate ring atoms occupy saddle points between peaks of *ca.* 0.05 eÅ^{-3}.

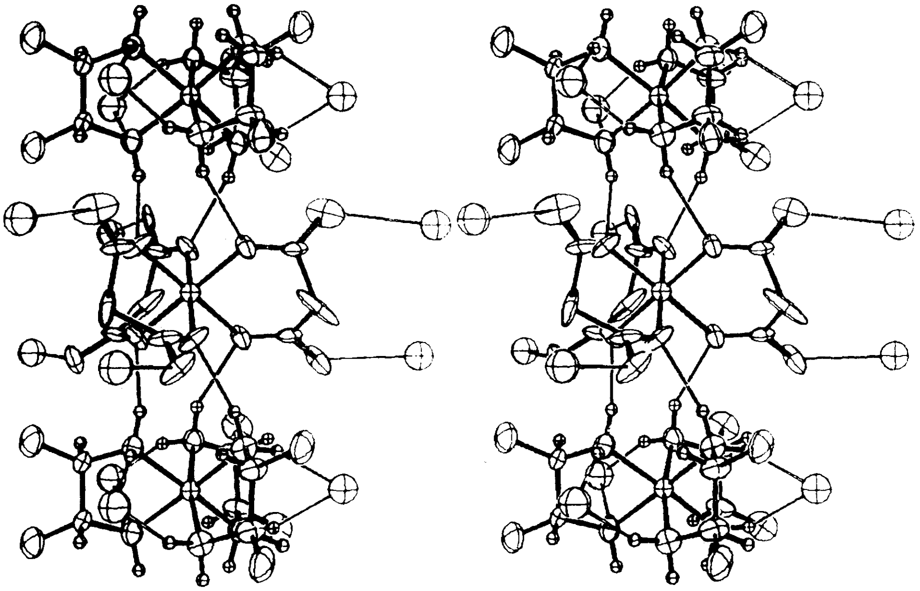

FIGURE 1 (−)[Co{(−)pn}$_3$](+)[Cr(mal)$_3$],3H$_2$O: Stereoscopic view of the arrangement viewed perpendicular to the *ac* plane

Of the 451 reflections listed in the structure-factor table [Supplementary Publication No. SUP 21432 (2 pp., 1 microfiche *)] 435 were included in the least-squares cycles. Those denoted E were excluded, mostly because of unsatisfactory determinations from the films, and those denoted *U* were unobserved and refined with their probable values. The weighting scheme was judged satisfactory from the final flat distribution of $w(|F_o| - |F_c|)^2$ averaged in ranges of $|F_o|$ *vs.* $|F_o|$. The final least-squares variables are given in Table 1. Atomic scattering factors for Co^{2+}, Cr^{2+}, and neutral light atoms were taken from ref. 31(*b*). Calculations were carried out on the University of Adelaide's CDC 64 000 with programs described in ref. 31(*c*).

RESULTS AND DISCUSSION

The Structure.—The structure consists of columns of alternating (+)Cr[(mal)$_3$]$^{3-}$ and (−)[Co{(−)pn}$_3$]$^{3+}$ complex ions hydrogen bonded together (Figure 1). The columns have three-fold symmetry and are connected by hydrogen bonds with water molecules. The molecular geometry is given in Table 2; Table 3 lists important intermolecular contacts. The trigonal complexes have opposite absolute configurations; (+)[Cr(mal)$_3$]$^{3-}$ has Λ absolute configuration by comparison with the known[32] Δ(λλλ) configuration of (−)[Co{(−)pn}$_3$]$^{3+}$. The equatorial N(1)H(2) hydrogen atoms each form a weak bifucated hydrogen bond with two ligator atoms of (+)[Cr(mal)$_3$]$^{3-}$, O(1) and its three-fold related oxygen O(1$^{\text{I}}$) (Table 3). Only the shortest and most linear bond is shown in Figure 1. These interactions do not account for the selectivity of the optical resolution since they could equally well exist with the ligator atoms of Δ(−)[Cr(mal)$_3$]$^{3+}$. In this context it is noted that the complexes (+)[Co(en)$_3$]$^{3+}$ and (−)[Co{(−)pn}$_3$]$^{3+}$ precipitate, and the former is an effective resolving agent for [M(ox)$_3$]$^{3-}$ complexes.[29b] The methyl group of Δ(−)-[Co{(−)pn}$_3$]$^{3+}$ cannot be responsible either since the same hand of (−)[Co(mal)$_3$]$^{3-}$ (Λ) has now been obtained with Δ(−)[Co(en)$_3$]$^{3+}$. The diastereoisomer is much more soluble in water in this case.[33] The selectivity of the resolution can be rationalised by considering hydrogen bonding with the water molecules between the complex-ion columns. The same complex ions in different columns are not adjacent, since their centres are shifted by the translational operations (0,0,0; $\frac{1}{3},\frac{2}{3},\frac{2}{3}$; $\frac{2}{3},\frac{1}{3},\frac{1}{3}$). The water molecule forms a pair of acceptor hydrogen bonds with the N(1)H(1) atoms of the (−)-[Co{(−)pn}$_3$]$^{3+}$ complex (Figure 1, Table 3) in one column as well as donor hydrogen bonds to both *exo*-oxygen atoms O(2) and O(3) of the malonate rings of (−)[Cr(mal)$_3$]$^{3-}$ in adjacent columns. Inversion of configuration at chromium would break the donor hydrogen bonds and give a destabilised structure.

Both complex ions are statistically disordered on 32 symmetry sites in the crystal. The *trans*(−)[Co{(−)-pn}$_3$]$^{3+}$ ion has no strict overall symmetry, but the non-

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

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methylated fragment does have 32 symmetry. Figure 2 shows the two half-occupied methyl sites. Table 3 shows two close contacts <3.1 Å of other atoms with these sites [C(2) $\cdots$ C(2^{II}) and O(2) $\cdots$ C(2^{III})]. As these other sites are also subject to disorder it is highly likely that the contacts are avoided in any particular unit cell. The cation has the tris-*lel*-conformation with the C–C bond of the pn ring parallel to the three-fold axis.

TABLE 2

Molecular geometry *

(*a*) Bond lengths (Å)

(i) Cation			
Co–N(1)	1.964(10)	C(1)–C(2)	1.50(4)
N(1)–C(1)	1.45(2)	C(1)–C(1′)	1.48(3)
(ii) Anion			
Cr–O(1)	1.953(7)	C(3′)–C(4)	1.61(4)
O(1)–C(3)	1.26(2)	C(3)–O(2)	1.33(5)
C(3)–C(4)	1.56(4) [a]	C(3′)–O(3)	1.20(5)

(*b*) Bond angles (°)

(i) Cation			
N(1)–Co–N(1′)	83.2(8)	N(1)–C(1)–C(2)	118(2)
Co–N(1)–C(1)	110.7(10)	C(2)–C(1)–C(1′)	115(1)
N(1)–C(1)–C(1′)	106.9(9)		
(ii) Anion			
O(1)–Cr–O(1′)	91.9(7)	O(1)–C(3)–C(4)	119(2)
Cr–O(1)–C(3)	128.3(9)	O(1′)–C(3′)–C(4)	114(1)
O(1)–C(3)–O(2)	122(2)	O(2)–C(3)–C(4)	118(2)
O(1′)–C(3)–O(3)	125(3)	O(3)–C(3′)–C(4)	118(3)
C(3)–C(4)–C(3′)	108(2)		

(*c*) Interligand angles at metal atoms

Symmetry operation relating donor atoms	cation	anion
3	90.3(4)	88.2(3)
2	97.1(10)	91.7(9)
32	170.2(11)	179.9(10)

* Primed atoms are related by a two-fold axis passing through the metal atoms relating to two halves of the chelate rings.

TABLE 3

Intermolecular contacts in crystal (<3.5 Å)

	X $\cdots$ Y		X $\cdots$ Y
C(1) $\cdots$ O(2)	3.42(3)	C(2) $\cdots$ C(2^{II})	3.06(8)
C(1) $\cdots$ O(3)	3.43(6)	N(1) $\cdots$ C(3^{I})	3.47(2)
N(1) $\cdots$ O(3^{I})	3.32(4)	O(2) $\cdots$ C(2^{III})	3.07(5)

Possible hydrogen bonds (X–H $\cdots$ Y)

	H $\cdots$ Y/Å	X $\cdots$ Y/Å	X–H $\cdots$ Y/°
N(1)–N(1)H(2) $\cdots$ O(1)	2.22	3.10(1)	154
N(1)–N(1)H(2) $\cdots$ O(1^{I})	2.50	3.24(2)	136
N(1)–N(1)H(1) $\cdots$ O(4^{I})	2.09	3.00(2)	155
O(4) $\cdots$ O(3)		3.18(4)	
O(4) $\cdots$ O(3^{II})		2.79(6)	
O(4) $\cdots$ O(2^{II})		2.67(4)	

Equivalent positions are shown by superior Roman numerals:

I $\bar{y}, x - y, z$ II $\frac{2}{3} - x, \frac{1}{3} + y - x, \frac{1}{3} - z$

III $\frac{2}{3} - y, \frac{1}{3} + x - y, \frac{1}{3} + z$

A tris(malonate) anion has 32 symmetry only if the methylene carbon [C(4)] lies on the two-fold axis through the metal ion, *i.e.* a completely flattened ring conformation or a symmetrical twist one. Here the five atoms Cr, O(1), O(1′), C(3), C(3′) are almost co-planar (Figure 3) with deviations of 0, −0.04, 0.04, 0.05, and −0.05 Å from their unweighted least-squares plane (equation $0.0X - 0.854Y - 0.535Z + 2.693 = 0$, where X, Y, and Z refer to orthogonal axes). The disordered methylene carbon half atom lies 0.71 Å from this plane; the ring conformation may be described as a boat (or chair) flattened at one end. The plane through the carbon atoms [C(3), C(4), C(3′), equation: $-0.767X - 0.554Y - 0.323Z + 3.629 = 0$] makes an angle of 50(3)° with that through the Cr, O(1), O(1)′ C(3), C(3)′ atoms given above. Only one of the disordered conformations is shown in Figure 3. The non-symmetry-related O(2) and O(3) sites are only 0.63(5) Å apart. As discussed earlier the anisotropic thermal ellipsoid of atom O(3) is non-positive definite and the minimum thermal ellipsoid shown in Figure 3 serves only to indicate its orientation. Its major axis is the direction of the disordered atom transformed by the two-fold axis and suggests a further disorder of O(3) along the axis which is inadequately approximated as a thermal motion. The

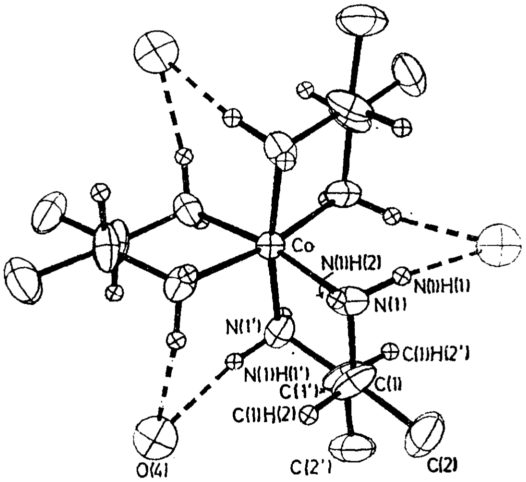

FIGURE 2 (−)[Co{(−)pn}$_3$] viewed down the *c* axis showing atom labelling and the disorder of the methyl groups. Atoms are drawn as 50% probability ellipsoids

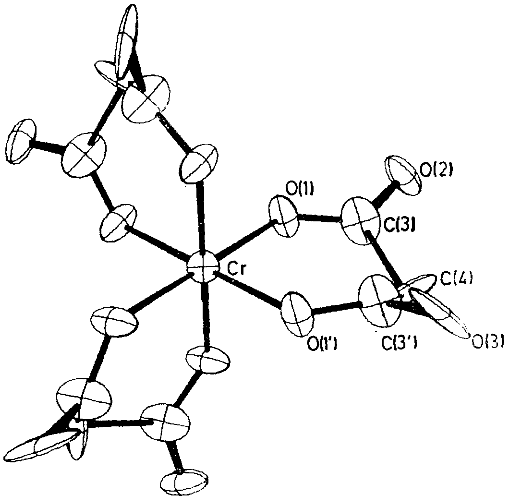

FIGURE 3 (+)Λ[Cr(mal)$_3$] viewed down the *c* axis showing the labelling scheme. For clarity the disorder of the O(2), C(4), and O(3) atoms is not shown. Atoms are drawn as 50% probability ellipsoids

Cr–O(1) bond length [1.953(7) Å] compares well with that found in $Cr(acetylacetone)_3$ [1.956(7)],[34] $Cr(glycinate)_3$ [1.964(1)],[35] and $(+)Cr\{(+)\text{-}3\text{-acetylcamphorate}\}_3$ [1.968(10) Å].[36] The O(1)—C(3) distance [1.262(18) Å] is the same as the mean of the carbonyl bonds [C(3)–O(2) 1.33(5) and C(3)–O(3) 1.20(5) Å], but the wide range of the latter renders comparison meaningless. Similarly the large uncertainty in the position of the methylene carbon C(4) precludes detailed discussion of the bond lengths and angles involved. Relevant to the theoretical evaluation of the c.d. spectra is the geometry of the CrO_6 core which has rigorous 32 symmetry. In addition to the Cr–O distance the geometry is defined by any two of the following angles: α, the chelate bite angle, 91.9(7)°; θ, the angle the O–Cr bond makes with the three-fold axis, 53.5(2)°; ω the angle O(1)–Cr–O(1′) projected on the plane perpendicular to the three-fold axis, 60.2(5)°. A regular octahedron has α 90, θ 54.75, and ω 60°.

The conformation of the malonate ring described here differs considerably from that reported[18] for $Na(+)[Co(en)(mal)_2],2H_2O$ where both rings adopt a boat conformation, and for $(-)[Co(NO_2)_2(en)_2](+)[Co(en)(mal)_2]$, where the malonate rings of the same anion adopt a flattened conformation.[37] The malonate conformation is thus highly dependent on its environment; this question is discussed in detail elsewhere.[38]

Absolute Configuration and Spectra.—The foregoing structure analysis has shown $(+)_{589}[Cr(mal)_3]^{3-}$ to have the Λ absolute configuration. This assignment is contrary to an earlier assignment based on an aqueous-solution c.d. spectrum.[12,39] The spectrum reported here (Figure 4 and Experimental section) is very similar except that the $(\varepsilon_l - \varepsilon_r)$ values of the peaks are 50—100% greater and a small new peak at 372 nm was found. The earlier assignment of configuration was based on the sign of the E_a symmetry component of the long wavelength ${}^4A_{2g}\rightarrow{}^4T_{2g}$ (O_h) transition.[12] The assignment of the E_a component in the solution c.d. spectrum was based on a single-crystal polarised absorption spectrum of $[Cr(mal)_3]^{3-}$ diluted in an $(NH_4)_3[Fe(mal)_3]$ crystal of unknown structure.[40] The negative component at 620 nm was assigned as E_a and the rule [12] that a positive E_a component arises from a complex of Λ configuration was applied to yield the incorrect Λ configuration $(-)_{589}[Cr(mal)_3]^{3-}$. In view of the unknown host lattice structure and the observation that the energy ordering need not be the same in solution as in a particular crystal lattice the above assignment of components is equivocal.[41]

The sign patterns of the c.d. spectra under the long wavelength transition [${}^4A_{2g}\rightarrow{}^4T_{2g}$ (O_h) for chromium(III) or ${}^1A_{1g}\rightarrow{}^1T_{1g}$ for cobalt(III)] fall predominantly into two classes for tris-chelate complexes of the same absolute configuration. Thus the pattern exhibited by $(-)\Delta[Cr(mal)_3]^{3-}$ is also shown by $(+)_{546}\Delta Co(acetylacetonate)_3$,[42] ΔCo and $Cr(3\text{-acetylcamphorate})_3$,[43] $(+)\Delta Co$ and $[Cr(biguanide)_3]Cl_3$,[16] and $K_3(-)\Delta[Cr(oxalate)_3]$.[12,18] The reversed pattern of component signs, of which $(+)\Delta[Co(mal)_3]^{3-}$ is an example, is shown by $(-)\Delta[Co(pn)_3]^{3+}$ and other five-membered diamine complexes.[44] The complex $(+)\Delta[Co(trimethylenediamine)_3]^{3+}$ also has this pattern although here the two components have been

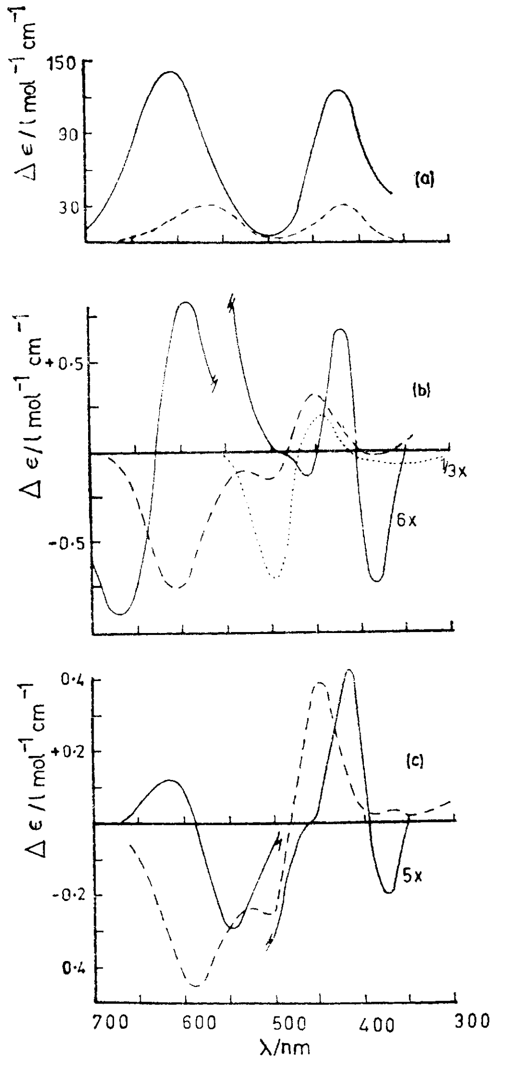

FIGURE 4 (a) Absorption spectra of $K_3[Co(mal)_3]$ (full line) and of $K_3[Cr(mal)_3]$ (dashed line) in water; (b) c.d. spectra of $(+)_{600}\Delta[Co(mal)_3]^{3-}$ (full line), $(-)\Delta[Co\{(-)pn\}_3]^{3+}$ (dotted line) in water and $(-)\Delta[Co(mal)_3](-)\Delta[Co\{(-)pn\}_3],3H_2O$ (dashed line) 2% in KBr on an arbitrary scale; (c) c.d. spectra of $(-)\Delta[Cr(mal)_3]^{3-}$ (full line) in water, and $(+)\Lambda[Cr(mal)_3](-)\Delta[Co\{(-)pn\}_3],3H_2O$ (dashed line) 2% in KBr on an arbitrary scale

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ascribed to two distinct conformers.[45,46] Other species such as $(+)\Delta[Co(oxalate)]^{3-}$ and $(-)[Cr(trimethylenediamine)_3]^{3+}$ exhibit only a single peak in this region of the spectrum.[12,47] The chromium and cobalt malonate species reported here are notable in that they are the only pair of complexes of these metals whose absolute configurations are known and which show reversed sign patterns. The sign pattern in this region is therefore not a reliable criterion for the assignment of absolute configuration. Such a pattern reversal can be explained by a reversal of the energy sequence of the E_a and A_2 components. For six-membered ring systems a reversal is suggested in an early correlation for trigonal complexes by Burer.[48] However, in view of the unsatisfactory nature of the component assignments and the possibility of alternative explanations, this correlation cannot be regarded as being substantiated by this study. Correlations between the geometry of the ML_6 chromophore and the signs and positions of the c.d. components have also been reported elsewhere [15] for oxalate, dithiooxalate, and malonate complexes. For $[Cr(mal)_3]^{3-}$, the value for the ω angle, 60.2(5)°, found here is close to the nodal value of 60° and optical activity arising from the CrO_6 chromophore would be expected to be very small from theory.[49] For $[Cr(ox)]_3{}^{3-}$ the c.d. differential extinction coefficients are an order of magnitude larger [12] and the ω angle is 50.3°.[15]

Figure 4 also shows the spectra of the diastereoisomers $[M(mal)_3][(-)Co\{(-)pn\}_3]$, measured as 2% dispersions pressed in KBr discs. These were made in the hope that since the structure in the solid is known they might clarify the interpretation of the solution c.d. spectra. The c.d. components of the ${}^1T_{1g}$ (O_h) transition centred on the absorption at 468 nm for $(-)[Co\{(-)pn\}_3]^{3+}$ are well separated from the corresponding components in the c.d. spectrum of $(+)[Co(mal)_3]^{3-}$ [Figure 4(b)]. In the c.d. disc spectrum of $(-)[Co(mal)_3](-)[Co\{(-)pn\}_3]$ the pair of components in the solution spectrum of $(+)[Co(mal)_3]^{3-}$ are replaced by a single peak and the relative intensities of the $(-)[Co\{(-)pn\}_3]^{3-}$ components are reversed. This latter effect is also evident in the c.d. disc spectrum of $(+)[Cr(mal)_3](-)[Co(-)pn_3]$. The observed enhancement of the A_2 component rotatory strength relative to that of E_a in the aqueous solution c.d. spectrum of $(-)[Co(en)_3]^{3+}$ and $(-)[Co\{(-)pn\}_3]^{3+}$ on the addition of oxy-anions such as phosphate and selenite has been rationalised [50,51] in terms of hydrogen bonding by the anion to the trigonal faces of the cation. More recently this suggested bonding scheme has been found in the crystal structure of $[Co(en)_3]_2(HPO_4)_3,9H_2O$.[52] The same kind of hydrogen bonding scheme is operative in the crystal structure of the diastereoisomers. On this basis the $(+)[Cr(mal)_3](-)[Co\{(-)pn\}_3]$ diastereoisomer peaks at 505 nm (—) and 450 nm (+) can be interpreted as being derived from the E_a and A_2 components of the ${}^1T_{1g}$ transition of $(-)[Co\{(-)pn\}_3]^{3+}$.

In the region of the $[M(mal)_3]^{3-}$ (M = Co or Cr) long wavelength transitions the c.d. spectra of the diastereoisomers both show only a single negative peak near 600 nm for the same absolute configuration. The intensity of these peaks relative to those assigned earlier to $(-)[Co\{(-)pn\}_3]^{3+}$ is much larger than would be expected on summing the components of the separate solution spectra of the anion and cation. The same effect is seen in solutions of $(+)_{600}\Delta[Co(mal)_3]^{3-}$ on dissolving successive amounts of $(+)\Lambda[Co(en)_3]Cl_3$ (Figure 5). The solution c.d. spectrum is unchanged by added KSCN or $CoCl_2$, $6H_2O$ showing that the peaks are not due to bridged species [26] involving $Co^{2+}{}_{aq}$ ions. Ammonium chloride produced no change in the spectrum which might have been expected if hydrogen-bonded ion pairs were formed.

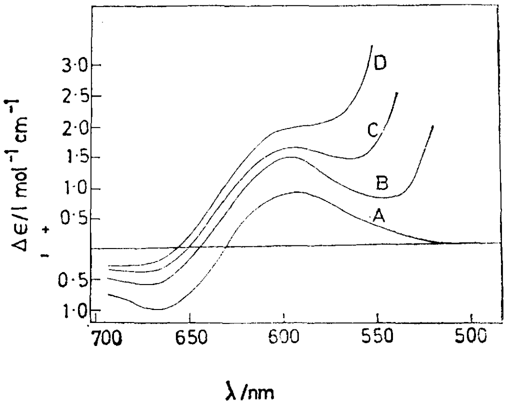

FIGURE 5 The c.d. spectra of $K_3(+)\Delta[Co(mal)_3]$ (0.02M) showing the effect of added solid $(+)[Co(en)_3]Cl_3$ to make the solution A, 0.0; B, 0.01; C, 0.06; and D, 0.2M in $(+)[Co(en)_3]Cl_3$

It is known that oxy-anions such as $[PO_4]^{3-}$ produce significant spectral changes of the above type with both conformationally rigid and labile tris(diamine)cobalt(III) complexes. Such changes in optical activity have been ascribed to a vicinal contribution from the disymmetric nitrogen centres $[Co-N(H)H \cdots O]$ as well as a conformational contribution from the altered population of conformers. The former contribution is considered to be generally more important.[53] Figure 1 suggests that this factor could be important here, although the principal hydrogen-bond interaction (shown) is such as to make the atoms about the ligator oxygen [Cr, C(3), and $\cdots$H] nearly planar. However, the ligator oxygen also has a longer interaction with another hydrogen atom of the same type (Table 3).

The KBr disc c.d. spectrum of $K_3\Lambda(-)[Cr(mal)_3]$ was measured and found to have peaks (relative deflections in

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mm) at 559 nm (−190), 430 (+33), and 380 (−10) making it similar to the solution spectrum [Figure 4(b)], but for the absence of a positive peak near 620 nm. The opposite antipode in the diastereoisomer spectrum shows a large negative peak between the two long wavelength solution spectrum peaks [Figure 4(c)]. These differences could be accounted for by specific solid-state effects or differing complex configurations in the several phases.† To help evaluate the latter effect the spectra were obtained for the similar but conformationally rigid systems, $[M(ox)_3]_3^{3-}$ (M=Co or Cr). The c.d. KBr disc spectra of the diastereoisomers Λ(+)$[Co(en)_3]$Λ$[M(oxalate)_3]$ [M = (−)Co and (+)Cr] are shown in Figure 6 together with the solution c.d. spectra of the component complexes. The patterns in the long-wavelength regions are similar for corresponding disc and solution spectra. There is however a shift of peak maxima to shorter wavelength from solution to solid. Thus the maxima in the solution c.d. $[Co(oxalate)_3]^{3-}$ spectrum at 620 nm appears at 595 nm in the disc spectrum of the diastereoisomer. This effect is not entirely due to the nature of the diastereoisomer, as a disc spectrum of K_3Λ[(−)Co(oxalate)$_3$] in KBr has this peak at 611 nm. This spectrum is otherwise similar to the solution spectrum shown in Figure 6. Analogous shifts of the maxima in the [(+)Cr(oxalate)$_3$]$^{3-}$ spectrum are also evident.

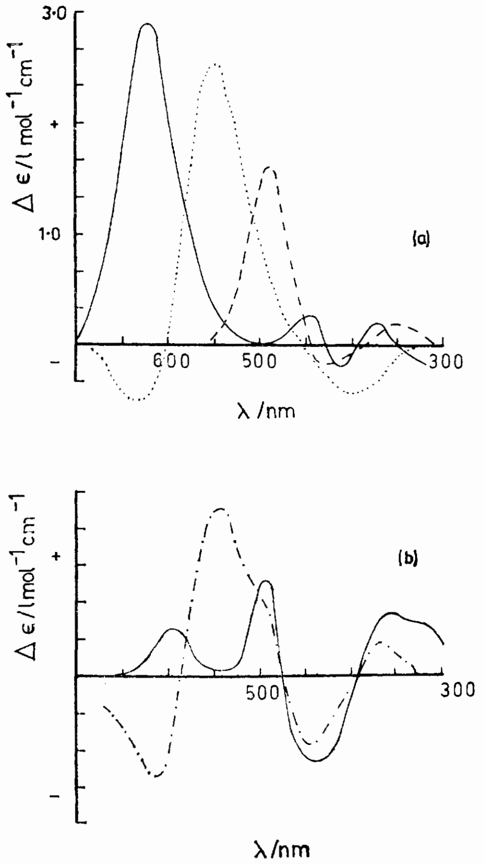

FIGURE 6 The c.d. spectra of (a) (−)Λ$K_3[Co(ox)_3]$ (full line), (+)Λ$K_3[Cr(ox)_3]$ (dotted line), and (+)Λ$[Co(en)_3]Cl_3$ (dashed line) in water, and (b) of (−)Λ$[Co(ox)_3]$(−)Λ$[Co(en)_3]$ (full line) and (+)Λ$[Cr(ox)_3]$(+)Λ$[Co(en)_3]$ (dash-dot line) as 2% in KBr discs on an arbitrary scale

Generally the diastereoisomer spectra are again not the simple sums of the component solution spectra. Even where the overall pattern might be anticipated the changes in relative intensities of the peaks can be large as for example with Λ$[Co(ox)_3]$Λ$[Co(en)_3]$. It appears likely that the cations are influencing the spectral regions of the anions in a similar manner to that previously established for polarisible anions and optically active cations.[53] The changes in spectra observed between solution and diastereoisomer can therefore not be readily interpreted in stereochemical terms. Recently the chiroptical properties of Λβ[Co(amino-acid)$_3$] complexes have been observed to alter with solvent and phase.[54] These complexes are capable of self-hydrogen-bonding since the amino-function and carboxy-groups are present in the same complex. It seems probable therefore that these spectra have the same origin as the ones reported here.

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† It is improbable that the solution c.d. of the tris(malonate) species is due to chemical equilibria involving ring opened species. The rapid and total precipitation of the pure diastereoisomer from solution is unlikely to allow reversal of any chemical equilibrium for the kinetically inert cobalt and chromium complexes. Ion-exchange chromatography does show minor components in the cobalt and chromium malonate systems, but these are stable and narrow and do not equilibrate in the 30 min required to run c.d. spectra of the solutions.

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