Crystal Structure and Absolute Configuration of (−)-Tris(pentane-2,4-dionato)chromium(III)

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The crystal structure and absolute configuration of the title complex (−)[Cr(pd)$_3$] has been determined from single-crystal *X*-ray data and refined by least-squares methods to *R* 0.037. The red-purple crystal has unit-cell dimensions $a = 12.720(3)$, $b = 12.643(4)$, $c = 11.443(3)$ Å, $\beta = 101.08(4)°$, space group $P2_1$, and $Z = 4$. The (−) isomer has the Δ configuration and a nearly regular CrO$_6$ co-ordination octahedron. The packing modes of the molecules in the *active* and in the *racemic* [Cr(pd)$_3$] crystal are compared and the enantiomeric discrimination in favour of the latter structure is analyzed.

THE present work reports an *X*-ray diffraction study of the crystal and molecular structure, including a determination of the absolute stereochemical configuration, of the (—) isomer of tris(pentane-2,4-dionato)chromium(III) which has become available in quantity recently, through an asymmetric synthesis.[1] The principal aims of the study are, first, an investigation of the expectation, based on circular dichroism (c.d.) spectroscopy, that (—)[Cr(pd)$_3$] has the right-handed Δ configuration [1] and, secondly, a comparison of the molecular packing in the *active* crystal with that in the corresponding *racemic* crystal, which has been previously determined.[2]

The latter objective refers to the problem of chiral discrimination.[3,4] An assembly of a given enantiomer of a particular chemical species generally has a higher intermolecular energy than that of the corresponding racemic assembly, and only some 200 cases are known of spontaneous optical resolution by crystallization either from the melt or from solution.[5] A racemate generally has a higher melting point and a lower solubility in a given solvent than the corresponding enantiomer. These differences derive from the differential in the lattice energy which is expected to be reflected in the mode of packing of the chiral molecules in the respective crystals.

Particular interest attaches to conformationally rigid enantiomers of high symmetry, for it has been noted that the spontaneous optical resolution by crystallization of chiral molecules with C_2 or higher symmetry is approximately twice as frequent statistically as the corresponding resolution of conformationally labile molecules devoid of elements of symmetry.[6] The highest chiral symmetry readily accessible experimentally is D_3, notably in tris(chelate) metal complexes having octahedral co-ordination. The crystal structures available [7] for a D_3 enantiomer and the corresponding racemic complex refer to charged species, and the two structures are not directly comparable, owing to differences of composition, *e.g.* [Co(en)$_3$]Cl$_3$·3H$_2$O [8] and Λ(+)[Co(en)$_3$]Cl$_3$·H$_2$O [9] (en = ethylenediamine), as well as to the contribution of the counterion to the packing mode.

Accordingly, attention has been directed to neutral D_3 metal complexes free from solvent of crystallization, notably the complexes [M(pd)$_3$] where M is a trivalent transition-metal ion and pd = pentane-2,4-dionate (acetylacetonate). Crystal structures for a number of racemic [M(pd)$_3$] complexes have been reported,[10,11] among which M = Al, Cr, Mn (β form), Co, and Rh pack in isomorphous monoclinic structures, and M = Sc, V (α form), Mn (α form), and Fe form another isomorphous series with an orthorhombic structure.[12] An *X*-ray diffraction study of Λ(—)[Co(pd)$_3$] doped into *rac*-[Al(pd)$_3$], undertaken to determine the absolute configuration of (—)[Co(pd)$_3$], has been reported, but the lattice parameters, and thus the mode of packing, are those of the racemic host crystal.[13] The absolute configuration of the (+)-3-acetylcamphorato-complex, Λ(+)-*trans*-[Cr{(+)atc}$_3$], has been determined by *X*-ray analysis,[14] providing a basis for the spectroscopic assignment [1] of the Δ configuration to (—)[Cr(pd)$_3$].

EXPERIMENTAL

Red-purple crystals of (—)[Cr(pd)$_3$] were obtained from the later fractions of the recrystallization of the product from the partial asymmetric synthesis described previously,[1] employing n-hexane–benzene (4 : 1) as the solvent. Crystals of the corresponding racemate were also produced and, in the case of the smaller crystals required for diffraction studies, the two types were not readily distinguished morphologically under the microscope. However, the densities of the active and racemic crystals are 1.28 and 1.36 g cm^{-3}, respectively, and they are separable with 2.5 mol dm^{-3} aqueous CsCl (density 1.316 g cm^{-3} at 20 °C). The two types of crystal are unambiguously identified by *X*-ray photography, the lattice parameters of *rac*-[Cr(pd)$_3$] being reported [2] as $a = 14.031$, $b = 7.551$, $c = 16.379$ Å, $\beta = 99.06°$, and space group $P2_1/c$.

Unit-cell dimensions were determined from Weissenberg photographs and were subsequently refined on a diffractometer.

Crystal Data.—(—)[Cr(pd)$_3$], C$_{15}$H$_{21}$CrO$_6$, $M = 349.3$, Monoclinic, $a = 12.720(3)$, $b = 12.643(4)$, $c = 11.443(3)$ Å, $\beta = 101.08(4)°$, $U = 1\,805.95$ Å^3, $D_m = 1.28$ (by flotation), $Z = 4$, $D_c = 1.285$ g cm^{-3}, $F(000) = 732$, Mo-K_α radiation, $\lambda = 0.710\,7$ Å, μ(Mo-K_α) = 6.6 cm^{-1}, space group $P2_1$.

Intensities were measured with Mo-K_α radiation on a Nonius CAD-4 automatic diffractometer operated in the θ—2θ scan mode up to $2\theta = 60°$, employing a spherically ground (diameter 0.3 mm) crystal specimen. Of the 3 322 unique observed reflections, 2 559 with $|F_o| \geqslant 3\sigma$ were used for the refinement. No absorption corrections were made to the intensity data.

Structure Determination.—Since $Z = 4$ in the space group $P2_1$ there are two independent molecules (I and II) in the asymmetric unit, requiring the location of 44 atoms, apart from the hydrogen atoms. The Patterson map showed a uniquely strong peak at ($\frac{1}{2}$, 0, $\frac{1}{2}$) with a peak height approximately one half of that at the origin. The chromium atoms were placed to account for this singular peak at Cr(1) (0.385, 0.0, 0.119) and Cr(2) (0.88, 0.01, 0.63), these locations being also consistent with other prominent peaks in the Patterson map. The strong correlation between the two types of chromium atom limited a straightforward heavy-atom determination of the structure.

TABLE 1

Fractional atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

	X	Y	Z
Molecule (I)			
Cr(1)	4 016(1)	43(1)	1 300(1)
O(11)	5 307(3)	907(4)	1 570(4)
O(12)	4 292(3)	−425(4)	−247(4)
O(13)	2 696(3)	−800(4)	1 077(4)
O(14)	3 753(3)	465(4)	2 868(3)
O(15)	4 867(4)	−1 180(4)	1 997(4)
O(16)	3 172(3)	1 246(3)	540(3)
C(11)	6 070(6)	850(7)	982(7)
C(12)	5 202(6)	−357(6)	−568(6)
C(13)	2 597(6)	−1 753(6)	1 388(6)
C(14)	3 181(5)	1 223(5)	3 085(5)
C(15)	4 501(7)	−2 115(7)	2 115(6)
C(16)	2 678(5)	1 914(5)	1 046(6)
C(17)	6 057(5)	207(6)	−9(6)
C(18)	2 646(5)	1 930(6)	2 249(6)
C(19)	3 460(7)	−2 398(7)	1 871(7)
M(11)	7 019(6)	1 544(8)	1 451(7)
M(12)	5 246(6)	−977(7)	−1 703(6)
M(13)	1 485(6)	−2 170(7)	1 200(8)
M(14)	3 054(5)	1 296(6)	4 365(5)
M(15)	5 387(7)	−2 898(7)	2 514(7)
M(16)	2 056(6)	2 731(6)	257(7)
Molecule (II)			
Cr(2)	8 845(1)	−119(1)	6 382(1)
C(21)	8 922(3)	139(3)	8 090(3)
O(22)	10 343(3)	297(3)	6 528(3)
O(23)	8 781(3)	−394(3)	4 681(3)
O(24)	7 344(3)	−580(3)	6 164(3)
O(25)	9 330(3)	−1 571(3)	6 782(3)
O(26)	8 367(3)	1 336(4)	5 985(4)
C(21)	9 796(4)	183(5)	8 867(4)
C(22)	11 047(4)	292(5)	7 481(5)
C(23)	9 075(5)	−1 225(5)	4 240(5)
C(24)	6 560(4)	−119(6)	5 489(5)
C(25)	9 601(4)	−2 254(4)	6 078(5)
C(26)	7 449(5)	1 595(5)	5 372(5)
C(27)	10 816(4)	216(5)	8 615(5)
C(28)	9 474(5)	−2 134(5)	4 852(6)
C(29)	6 602(5)	913(6)	5 078(6)
M(21)	9 665(5)	245(6)	10 150(5)
M(22)	12 181(5)	421(5)	7 333(5)
M(23)	8 933(7)	−1 216(7)	2 887(6)
M(24)	5 558(5)	−762(5)	5 165(5)
M(25)	10 044(5)	−3 261(5)	6 667(6)
M(26)	7 342(5)	2 749(6)	5 009(6)

Twelve peaks appeared around each chromium location in the Fourier synthesis based on the phase relation between the two types of chromium atom, corresponding to the six oxygen atoms of the co-ordination octahedron doubled by pseudo-mirror planes. The chromium atom and the peaks for the oxygen atoms of molecule (I) and of molecule (II) were related by the vector ($\frac{1}{2}$, 0, $\frac{1}{2}$).

Two sets of co-ordinates for the CrO_6 co-ordination octahedron were feasible for each of the two independent molecules, due to the 12 observed oxygen peaks in each case, giving four possible combinations. Several cycles of least-squares refinement were carried out with each of the four pairs of co-ordinate sets for the independent CrO_6 clusters, but convergence was limited to $R \simeq 0.34$ in each case. Fourier and difference-Fourier maps revealed fragments of the chelate rings and peaks corresponding to the methyl carbon atoms. Least-squares refinements including these carbon atoms did not reduce the R factor below 0.28 for any of the four pairs of CrO_6 co-ordinate sets, and no other carbon atoms emerged from the subsequent Fourier or difference-Fourier synthesis. No improvement was achieved by the introduction of a damping factor to reduce the strong correlation between the two types of chromium atom, or through attempts to break the pseudo-symmetry by minor co-ordinate shifts or the input of partial CrO_6 structures.

At this stage the possible packing modes of (−)[Cr(pd)$_3$] in the unit cell were examined by means of molecular models, which included the van der Waals radii of the hydrogen atoms, on the assumption that the CrO_6 co-ordination octahedra had been correctly located. Owing to intermolecular contacts between nearest-neighbour atoms the number of feasible mutual orientations of the molecules in the unit cell appeared to be severely limited. With the first trial structure selected from the packing modes suggested by the molecular models, all the atoms heavier than hydrogen were located by Fourier synthesis and least-squares refinement, R being reduced to 0.059 using anisotropic temperature factors. The positions of the hydrogen atoms located by the difference-Fourier synthesis obtained at this stage were in satisfactory agreement with the corresponding idealised positions.

A final full-matrix least-squares refinement was carried out with all the hydrogen atoms placed at their idealised bonded positions while allowing each methyl group to rotate about the C–C bond to the chelate ring. Isotropic and anisotropic temperature factors were adopted for the hydrogen atoms and for the heavier atoms, respectively, and the structure was refined in two separate blocks for molecule (I) and molecule (II) individually. A correction was made for the anomalous scattering due to the chromium atom and equal weight was assigned to each reflection. The final R value was 0.037. The atomic scattering factors for the heavy atoms and for the hydrogen atoms were taken from refs. 15 and 16, respectively. Calculations were carried out by means of the University of London CDC 7600 computer using the program SHELX, written by Dr. G. Sheldrick. The final set of atomic co-ordinates is listed in Table 1. Observed and calculated structure amplitudes and the thermal parameters of the atoms are tabulated in Supplementary Publication No. SUP 22388 (14 pp.).[*]

TABLE 2

Determination of the absolute configuration. Relations between $|F_c(hkl)|^2$ and $|F_c(h\bar{k}l)|^2$ observed and calculated for the Δ configuration

h	k	l	$\lvert F_c(hkl)\rvert^2$	observed	$\lvert F_c(h\bar{k}l)\rvert^2$
$\bar{3}$	1	3	1 600	>	900
1	1	3	961	<	1 600
1	3	3	324	>	121
3	1	3	81	>	1
3	2	3	144	>	0
6	2	3	625	>	441
9	1	3	25	<	100
2	1	4	576	>	144
4	1	4	256	<	625
4	2	4	441	>	169

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[*] For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

Determination of the Absolute Configuration of the Complex.—Equi-inclination Weissenberg photographs were taken of the third and fourth layers around the crystal *c* axis with Fe-K_α radiation ($\Delta f' = -1.973$, $\Delta f'' = 3.533$). The relations between $|F_c(hkl)|^2$ and $|F_c(h\bar{k}l)|^2$ calculated for the Δ configuration of the complex are compared (Table 2) with the corresponding observed relations. The comparison indicates unambiguously that (−)[Cr(pd)$_3$] has the Δ configuration, as was previously assigned by c.d. spectroscopy.[1,17]

TABLE 3

Intramolecular bond lengths (Å) and angles (°)

Molecule (I)		Molecule (II)	
Cr(1)–O(11)	1.947(5)	Cr(2)–O(21)	1.965(3)
Cr(1)–O(12)	1.961(4)	Cr(2)–O(22)	1.953(4)
Cr(1)–O(13)	1.964(4)	Cr(2)–O(23)	1.963(4)
Cr(1)–O(14)	1.962(4)	Cr(2)–O(24)	1.966(4)
Cr(1)–O(15)	1.966(5)	Cr(2)–O(25)	1.963(4)
Cr(1)–O(16)	1.965(4)	Cr(2)–O(26)	1.963(5)
O(11)–C(11)	1.285(9)	O(21)–C(21)	1.284(6)
O(12)–C(12)	1.282(9)	O(22)–C(22)	1.271(6)
O(13)–C(13)	1.270(9)	O(23)–C(23)	1.254(8)
O(14)–C(14)	1.256(8)	O(24)–C(24)	1.278(6)
O(15)–C(15)	1.287(10)	O(25)–C(25)	1.273(7)
O(16)–C(16)	1.258(8)	O(26)–C(26)	1.283(7)
C(11)–C(17)	1.393(11)	C(21)–C(27)	1.384(8)
C(12)–C(17)	1.353(10)	C(22)–C(27)	1.388(8)
C(14)–C(18)	1.388(9)	C(23)–C(28)	1.390(9)
C(16)–C(18)	1.385(10)	C(25)–C(28)	1.389(9)
C(13)–C(19)	1.393(11)	C(24)–C(29)	1.391(11)
C(15)–C(19)	1.349(12)	C(26)–C(29)	1.371(9)
C(11)–M(11)	1.506(11)	C(21)–M(21)	1.511(8)
C(12)–M(12)	1.527(10)	C(22)–M(22)	1.494(8)
C(13)–M(13)	1.485(11)	C(23)–M(23)	1.523(9)
C(14)–M(14)	1.506(9)	C(24)–M(24)	1.498(8)
C(15)–M(15)	1.503(2)	C(25)–M(25)	1.499(8)
C(16)–M(16)	1.495(10)	C(26)–M(26)	1.516(9)
O(11)–Cr(1)–O(12)	91.2(2)	O(21)–Cr(2)–O(22)	90.5(2)
O(13)–Cr(1)–O(15)	90.9(2)	O(23)–Cr(2)–O(25)	91.0(2)
O(14)–Cr(1)–O(16)	91.1(2)	O(24)–Cr(2)–O(26)	89.9(2)
Cr(1)–O(11)–C(11)	125.7(5)	Cr(2)–O(21)–C(21)	124.5(4)
Cr(1)–O(12)–C(12)	124.5(4)	Cr(2)–O(22)–C(22)	124.2(5)
Cr(1)–O(13)–C(13)	127.4(4)	Cr(2)–O(23)–C(23)	126.1(4)
Cr(1)–O(14)–C(14)	126.5(4)	Cr(2)–O(24)–C(24)	124.6(4)
Cr(1)–O(15)–C(15)	125.7(5)	Cr(2)–O(25)–C(25)	126.7(4)
Cr(1)–O(16)–C(16)	126.5(4)	Cr(2)–O(26)–C(26)	125.1(4)
C(11)–C(11)–C(17)	124.6(7)	O(21)–C(21)–C(27)	125.4(5)
O(12)–C(12)–C(17)	126.0(6)	O(22)–C(22)–C(27)	124.2(5)
O(13)–C(13)–C(19)	123.6(7)	O(23)–C(23)–C(28)	126.7(6)
O(14)–C(14)–C(18)	125.5(5)	O(24)–C(24)–C(29)	123.8(5)
O(15)–C(15)–C(19)	125.6(8)	O(25)–C(25)–C(28)	124.9(5)
O(16)–C(16)–C(18)	125.4(6)	O(26)–C(26)–C(29)	124.3(6)
O(11)–C(11)–M(11)	114.5(7)	O(21)–C(21)–M(21)	115.6(5)
O(12)–C(12)–M(12)	113.1(6)	O(22)–C(22)–M(22)	116.0(5)
O(13)–C(13)–M(13)	116.0(6)	O(23)–C(23)–M(23)	114.6(6)
O(14)–C(14)–M(14)	114.4(5)	O(24)–C(24)–M(24)	115.4(6)
O(15)–C(15)–M(15)	111.8(7)	O(25)–C(25)–M(25)	114.5(5)
O(16)–C(16)–M(16)	116.0(6)	O(26)–C(26)–M(26)	114.8(5)
C(17)–C(11)–M(11)	120.9(7)	C(27)–C(21)–M(21)	118.9(5)
C(17)–C(12)–M(12)	121.0(7)	C(27)–C(22)–M(22)	119.7(5)
C(19)–C(13)–M(13)	120.4(7)	C(28)–C(23)–M(23)	118.6(6)
C(18)–C(14)–M(14)	120.0(6)	C(29)–C(24)–M(24)	120.8(5)
C(19)–C(15)–M(15)	122.5(8)	C(28)–C(25)–M(25)	120.5(6)
C(18)–C(16)–M(16)	118.5(6)	C(29)–C(26)–M(26)	120.9(6)
C(11)–C(17)–C(12)	125.1(7)	C(21)–C(27)–C(22)	124.9(5)
C(14)–C(18)–C(16)	124.9(6)	C(23)–C(28)–C(25)	124.1(6)
C(13)–C(19)–C(15)	126.5(8)	C(24)–C(29)–C(26)	124.6(4)

DISCUSSION

The two independent molecules in the unit cell of Δ(−)[Cr(pd)$_3$] each approximate closely to D_3 symmetry (Figure 1). Corresponding intramolecular bond distances and bond angles in molecules (I) and (II) have similar values (Table 3) and do not differ significantly from those of the molecule in the racemic [Cr(pd)$_3$] crystal.[2] The CrO$_6$ co-ordination octahedron is nearly regular with an average intrachelate O–O distance or ' bite ' similar to the average corresponding interchelate distance within a molecule (Table 4). The Cr–O bonds are inclined at an average angle (θ) of 54.8° to the three-fold axis in each of the molecules (I) and (II), compared with $\theta = 54.75°$ for a regular octahedron. The averages of the azimuthal projection of the intrachelate O–Cr–O angles (ϕ) are 62.1 and 60.9° for molecule (I) and (II), respectively, while $\phi = 60°$ for the octahedron. For [Cr(pd)$_3$] in the racemic crystal,[2] $\theta = 54.6°$ and $\phi = 61.5°$. Thus the polar distortion of the CrO$_6$ co-ordination octahedron along the direction of the three-fold axis is insignificant, but the chelation produces a small expansion in the azimuthal plane. The atoms of each chelate ring in molecules (I) and (II) are sensibly coplanar, but the minor degree of ring puckering is the more evident in Δ(−)[Cr(pd)$_3$] than in the racemic crystal,[2] due to the lower symmetry of the packing mode in the former crystal.

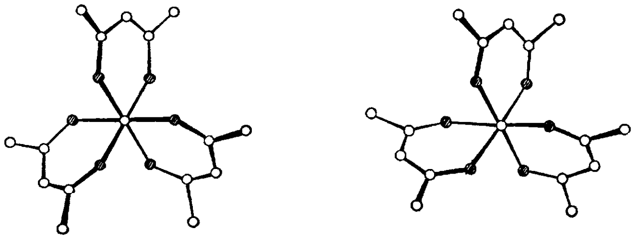
Molecule (I)
Molecule (II)

FIGURE 1 Structure of the two independent molecules in the unit cell of the Δ(−)[Cr(pd)$_3$] crystal

TABLE 4

Oxygen–oxygen distances (Å)

Molecule (I)		Molecule (II)	
(*i*) Intrachelate			
O(11)–O(12)	2.792	O(21)–O(22)	2.783
O(13)–O(15)	2.802	O(23)–O(25)	2.800
O(14)–O(16)	2.803	O(24)–O(26)	2.775
average	2.799	average	2.786
(*ii*) Interchelate			
O(11)–O(14)	2.749	O(21)–O(24)	2.830
O(11)–O(15)	2.760	O(21)–O(25)	2.735
O(11)–O(16)	2.778	O(21)–O(26)	2.817
O(12)–O(13)	2.798	O(22)–O(23)	2.750
O(12)–O(15)	2.706	O(22)–O(25)	2.733
O(12)–O(16)	2.792	O(22)–O(26)	2.798
O(13)–O(14)	2.740	O(23)–O(24)	2.733
O(13)–O(16)	2.752	O(23)–O(26)	2.755
O(14)–O(15)	2.805	O(24)–O(25)	2.787
average	2.764	average	2.771

Crystal Packing.—A comparison of the crystal structure of an enantiomer with that of the corresponding racemate reveals, in a number of cases,[18-20] packing features common to the two structures, either one- or two-dimensional in the form of either columns or layers of molecules with the same stereochemical configuration. Homochiral columns of molecules, common to the *active* and to the *racemic* crystal, have been found in an *X*-ray diffraction study[18] of (—)-*trans*-1,2-dibromoacenaphthene and of the corresponding racemic crystal. The spacing of the molecules along the homochiral columns and the packing in the orthogonal plane are closer for the active than the racemic crystal, resulting in densities of 1.52 and 1.38 g cm^{-3}, respectively.[18] The racemic crystals are only a little more stable thermodynamically than the conglomerate of corresponding active crystals, while the analogue *trans*-1,2-dichloroacenaphthene is spontaneously resolved into optical isomers by crystallization.[18] In the series of *trans*-cycloalkane-1,2-dicarboxylic acids[19] and of the α-amino-acids,[20] where spontaneous optical resolution by crystallization is less infrequent than elsewhere,[21] a two-dimensional homochiral packing is observed in layers common to the active and the corresponding racemic crystal.

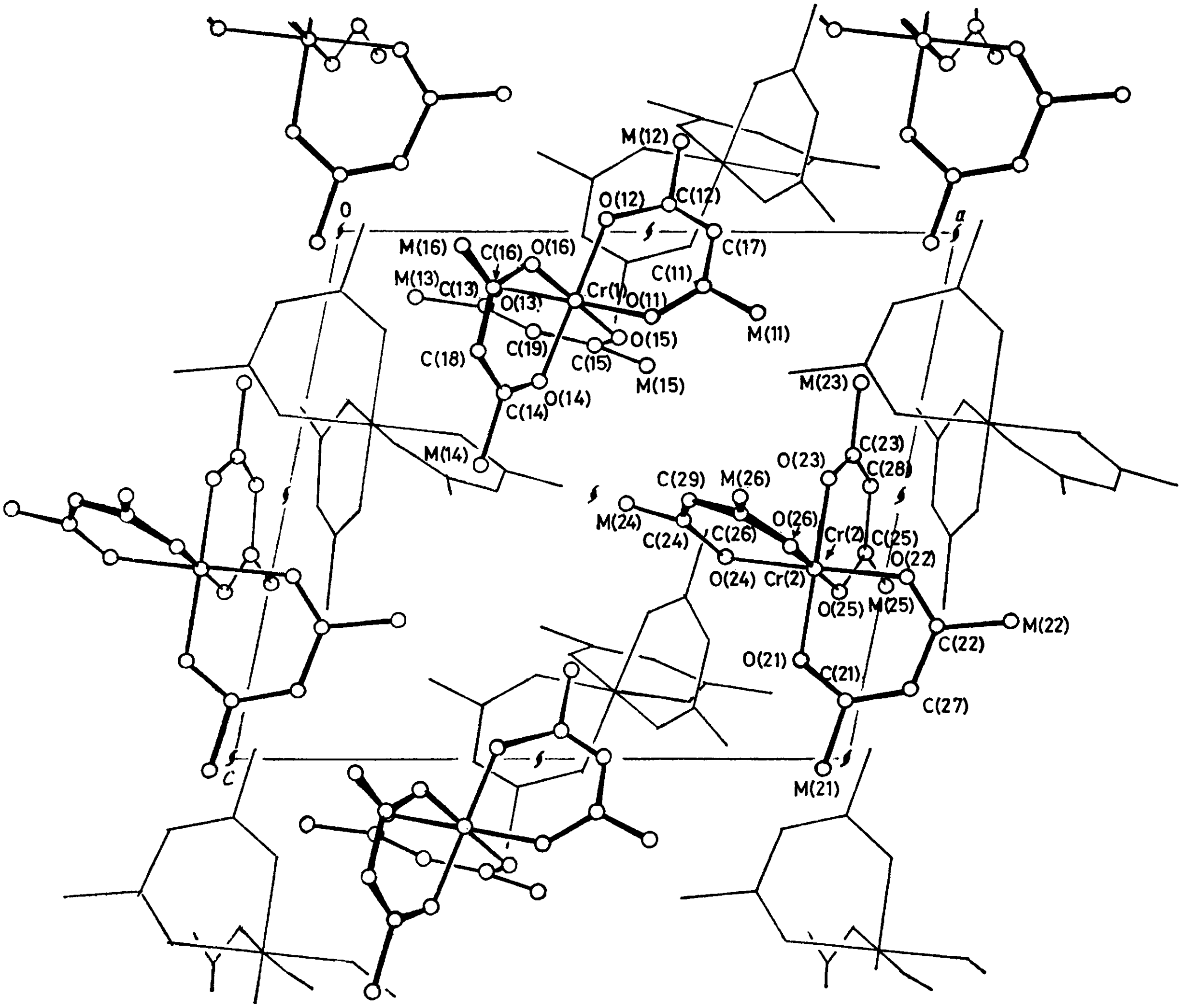

FIGURE 2 Projection of the Δ(—)[Cr(pd)$_3$] crystal structure on the *ac* plane viewed down the *b* axis. The heavier and lighter illustrations refer to molecules separated along the *b* axis by $y = \frac{1}{2}$

The packing modes of the active and of the racemic [Cr(pd)$_3$] crystal are found to be less closely related due, in part at least, to the different steric constraints imposed generally on the sequential pairwise packing of dihedral propeller-like structures with the same or with opposed chiralities. While the tris(chelate) complexes with D_3 symmetry stack efficiently in columns along a direction at a small angle or parallel to the individual molecular C_3 axes only if they have the same stereochemical configuration, these complexes pack economically in the orthogonal plane with parallel molecular C_3 axes only if adjacent molecules in the plane are racemic pairs with antipodal configurations. The packing allows the contiguous chelate rings of enantiomorphous neighbours in the orthogonal plane to assume a parallel mutual orientation. If the contiguous chelate rings of two adjacent molecules with the same configuration are superimposed with parallel C_2 axes, the two molecular C_3 axes become mutually orientated at the tetrahedral angle or its supplement (70.5°). Thus two parallel homochiral columns composed of tris(chelate) complexes stacked along or at a small angle to the molecular C_3

axes pack efficiently in the orthogonal plane if the two columns are enantiomorphous but not if they have a common chirality.

A projection along the *b* axis of the structure of the $\Delta(-)[\mathrm{Cr(pd)_3}]$ crystal on the *ac* plane is illustrated, with the numbering scheme (Figure 2), for comparison with the corresponding projection [2] of the racemic crystal structure. The angle between the molecular C_3 axes of each pair of the four molecules in the unit cell is listed (Table 5) for the active and for the racemic crystal. In the racemic crystal structure the *ac* plane of a unit cell is orthogonal to four homochiral columns of $[\mathrm{Cr(pd)_3}]$ molecules extending along the *b* axis with the C_3 axis of each molecule at ±30.7° to the *b* crystal axis. The four homochiral columns in the racemic crystal are made up of two pairs of antipodal columns. The C_3 axes of all the molecules within a given enantiomorphous column-pair are parallel to one another and lie at an angle of 61° to the direction of the molecular C_3 axes in the other column pair (Table 5). The enantiomorphous structure of the molecules forming a contiguous pair of homochiral columns, and the mutual orientation of the molecules in different column pairs, allows an interleaving of the chelate rings between adjacent columns [2] which has no close analogue in the molecular packing of the active crystal (Figure 2, Table 5).

TABLE 5

The observed angle between the C_3 rotation axes, and the distance between the chromium atoms, of nearest-neighbour molecules in the active and in the racemic $[\mathrm{Cr(pd)_3}]$ crystal. Molecules (I) and (II) are independent in the active crystal. Crystal-symmetry relations between adjacent molecules, and their relative stereochemical configuration, are denoted by the following superscripts: s = two-fold screw axis, same configuration; i = inversion centre, opposite configuration; b = *b*-axis translation, same configuration; and g = glide plane, opposite configuration

Molecule pair	C_3–C_3' angle/°	Cr ··· Cr distance/Å
$\Delta(-)[\mathrm{Cr(pd)_3}]$ ($P2_1$)		
(I)–(I^{s})	3.7	7.61
(I)–(II)	75.3	7.60, 7.79, 9.09
(I)–(II^{s})	73.0	7.84, 8.16
(II)–(II^{s})	74.5	7.88
rac-$[\mathrm{Cr(pd)_3}]$ *($P2_1/c$)		
(I)–(I^{b})	0	7.55
(I)–(I^{i})	0	7.74, 7.97, 8.09
(I)–(I^{g})	61.0	8.19
(I)–(I^{s})	61.0	9.79

* Data derived from ref. 2.

The four types of molecule in the unit cell of the $\Delta(-)[\mathrm{Cr(pd)_3}]$ crystal are the independent molecules (I) and (II) and their counterparts (I^{s}) and (II^{s}), respectively, related by the two-fold screw axis of the crystal. There are no columns of contiguous molecules of a particular type in the *active* crystal structure, analogous to the homochiral columns of the racemic crystal, owing to the interposition of molecules of a different type along each of the three axial directions in the crystal. Thus the *b*-axis unit-cell spacing in the active crystal (12.643 Å) is substantially larger than that (7.551 Å) of the racemic crystal where the *b*-axis interval corresponds to the intermolecular separation along a homochiral column. Although the molecules in the active crystal occupy a smaller cross-sectional area in the *ac* plane, the *b*-axis spacing dominates, and the structure of the racemic crystal is the more compact with a unit-cell volume [2] of 1 714 Å^3, compared with 1 806 Å^3 for the active crystal.

The C_3 axes of molecules (I) and (I^{s}) lie nearly in the *ac* plane of the active crystal, at an angle of ±88.1° to the *b* axis, with which the C_3 axes of molecules (II) and (II^{s}) make an angle of ±53.7°. While the C_3 axes of molecules (I) and (I^{s}) are almost parallel, lying only at an angle of 3.7° to one another, the other three angular relations between the C_3 axes of two molecules of different types in the active unit cell lie close to their average value of 74.3° (Table 5). This average corresponds to the sum (74.2°) of the supplement of the tetrahedral angle (70.5°) and the angle between the nearly parallel C_3 axes of molecules (I) and (I^{s}) (3.7°). Thus in the structure of the active crystal the steric requirements for efficient packing along a direction at a small angle to the molecular C_3 axis and in the orthogonal plane are competitive, and the condition for near-parallel contiguous chelate rings is dominant, requiring the tetrahedral angle or its supplement between the C_3 axes of neighbouring molecules. These steric requirements have a more complementary character for the racemate, which has the more compact and regular crystal structure. Thus the packing mode of the active crystal entails more close contacts between adjacent molecules in the lattice (Table 6) than those reported [2] for the racemic crystal, although the minimum separations are comparable for the two cases. The more compact structure of the racemic crystal results in a larger lattice energy, as is exemplified by the smaller solubility of the racemic than the active crystals in a range of common solvents.

TABLE 6

Intermolecular distances (nearest neighbours) (Å)

O(25) ··· C(18$^{\text{II}}$)	3.494	O(24) ··· C(18$^{\text{II}}$)	3.634
M(24) ··· O(14$^{\text{I}}$)	3.503	O(28) ··· O(26$^{\text{VI}}$)	3.636
O(21) ··· C(13$^{\text{III}}$)	3.560	C(28) ··· O(22$^{\text{VI}}$)	3.639
C(27) ··· O(13$^{\text{IV}}$)	3.566	M(24) ··· O(12$^{\text{VII}}$)	3.690
O(23) ··· M(25$^{\text{V}}$)	3.574	O(26) ··· M(13$^{\text{III}}$)	3.707
M(24) ··· O(15$^{\text{I}}$)	3.601	C(21) ··· M(13$^{\text{III}}$)	3.717
C(27) ··· O(16$^{\text{IV}}$)	3.604	M(12) ··· C(16$^{\text{VIII}}$)	3.726
M(22) ··· O(12$^{\text{IV}}$)	3.628	M(22) ··· M(15$^{\text{IX}}$)	3.729

I X, Y, Z
II $-X + 1, Y - \frac{1}{2}, -Z + 1$
III $-X + 1, Y + \frac{1}{2}, -Z + 1$
IV $X + 1, Y, Z + 1$
V $-X + 2, Y - \frac{1}{2}, -Z + 1$
VI $-X + 2, Y - \frac{3}{2}, -Z + 1$
VII $X, Y, Z + 1$
VIII $-X + 1, Y - \frac{3}{2}, Z$
IX $-X + 2, Y + \frac{1}{2}, -Z + 1$

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