Chiral Discriminations of Complexes with D_3 Symmetry. Molecular Structure and Crystal-packing Mode of $(-)_{589}$-Tris[(−)-*O,O'*-1(*R*),2(*R*)-dimethylethylene dithiophosphato]chromium(III), $[Cr\{(-)bdtp\}_3]$†

Reiko Kuroda *
Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro, Tokyo, 153 Japan
Paolo Biscarini
Dipartimento di Chimica Fisica ed Inorganica dell'Universita', Viale Del Risorgimento, 40136 Bologna, Italy

The molecular structure and crystal-packing mode of $[Cr\{(-)bdtp\}_3]$ [bdtp = *O,O'*-1(*R*),2(*R*)-dimethylethylene dithiophosphate] have been determined from single-crystal *X*-ray diffraction data and refined by full-matrix least-squares methods to *R* 0.0435. The optically active crystal has unit-cell dimensions a = 11.699(1), b = 12.738(2), c = 16.827(2) Å, space group $P2_12_12_1$ and Z = 4. The ligand has two ring planes: an inner four-membered chelate ring and an outer five-membered ring. The complex exhibits approximate D_3 symmetry and the three inner rings and the three outer rings each form a propeller of opposite handedness. The crystal-packing mode and the chiral recognitions have been compared with those of D_3 tris(chelate)metal complexes involving a single propeller system.

For chiral compounds the assembly of a given enantiomer generally has a higher intermolecular energy than that of the corresponding racemic species, and only some 200 cases are known of spontaneous optical resolution.[1] A racemic crystal usually has a higher melting point, a higher density and a lower solubility in a given solvent than the corresponding enantiomeric crystal. These differences derive from the differential mode of packing of the chiral molecules in the respective crystals.[2]

We have been particularly interested in conformationally rigid chiral compounds of high symmetry. The highest chiral symmetry readily accessible experimentally is D_3 notably tris(bidentate chelate)metal complexes having octahedral coordination. These complexes normally possess a propeller type structure and are optically active even though the ligands do not contain a chiral centre. One such example is the tris(ethylenediamine)cobalt(III) ion, $[Co(en)_3]^{3+}$, which exists in a right-handed propeller form, Δ, and in an enantiomeric left-handed propeller form, Λ. When these molecules, either in an optically active or racemic form, are packing in a crystal lattice the chirality is reflected by interactions among the propeller blades, and quite often these crystals adopt a unique packing mode.[3,4] We have calculated the chiral discrimination energies of model D_3 metal complexes, for both an active pair, Δ-Δ or Λ-Λ configurations, and a racemic pair, Δ-Λ configuration, on the basis of an extended transition monopole model.[3]

The complex $(-)_{589}$-tris[(−)-*O,O'*-1(*R*),2(*R*)-dimethylethylene dithiophosphato]chromium(III), $(-)$-$[Cr\{(-)bdtp\}_3]$, exhibits an interesting feature from the point of chiral discriminations/recognitions and the mode of crystal packing. It contains four-membered chelate rings and another five-membered ring is joined to each four-membered ring at the phosphorus atom (Figure 1). The phosphorus atom adopts a tetrahedral geometry and hence the two rings are expected to be almost perpendicular to each other. The result is that when the three inner rings form a right-handed propeller the outer rings necessarily form a left-handed propeller. The chromium complex is neutral and devoid of counter ions. Moreover, no solvent molecules are included in the crystal. Counter ions and solvent molecules generally contribute to the packing mode, complicating analysis of chiral recognition. The absence of these features for the chromium complex renders it an attractive system for investigation.

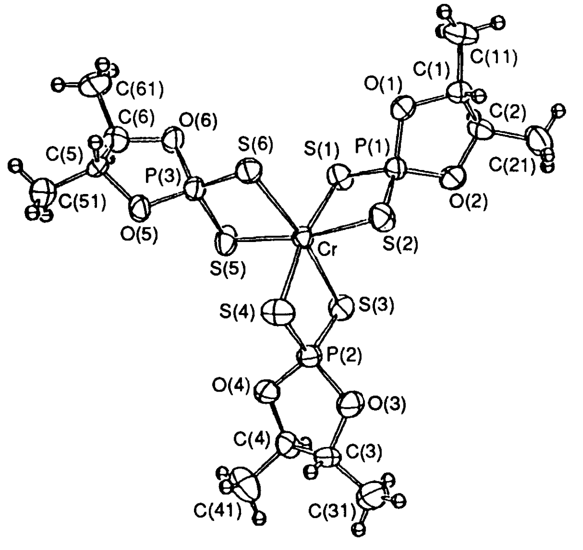

Figure 1. ORTEP drawing of the molecular structure Λ-$[Cr\{(-)_{589}bdtp\}_3]$ with the numbering scheme employed (50% probability thermal ellipsoids)

In this study, the molecular structure and the crystal packing mode of this complex have been determined and the packing mode compared with that of optically active D_3 complexes of simple propeller shape.

Experimental

It was extremely difficult to obtain crystals of reasonable size and good quality and numerous attempts had to be made over several years. The compound is optically labile as observed from

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Final atomic co-ordinates with estimated standard deviations in parentheses for [Cr{(−)bdtp}$_3$]

Atom	*x*	*y*	*z*
Cr	0.749 1(2)	0.007 6(1)	0.249 7(1)
S(1)	0.585 2(1)	0.124 1(2)	0.249 7(2)
S(2)	0.740 4(3)	0.039 5(2)	0.108 7(2)
S(3)	0.625 5(2)	−0.145 3(2)	0.249 2(2)
S(4)	0.895 5(3)	−0.126 4(2)	0.231 3(2)
S(5)	0.757 1(3)	0.007 3(3)	0.393 6(2)
S(6)	0.887 4(3)	0.147 2(2)	0.266 0(2)
P(1)	0.610 9(3)	0.132 8(2)	0.134 0(2)
P(2)	0.769 5(2)	−0.227 3(2)	0.246 5(2)
P(3)	0.874 0(3)	0.118 3(2)	0.380 8(2)
O(1)	0.626 3(7)	0.251 6(6)	0.105 5(4)
O(2)	0.502 4(7)	0.106 1(6)	0.080 8(5)
O(3)	0.763 6(8)	−0.319 0(6)	0.182 3(4)
O(4)	0.788 9(7)	−0.299 3(6)	0.323 2(4)
O(5)	0.992 4(6)	0.087 3(6)	0.422 0(4)
O(6)	0.849 8(6)	0.222 4(6)	0.429 7(5)
C(1)	0.555(1)	0.275 5(8)	0.036 1(6)
C(2)	0.457(1)	0.200 0(8)	0.042 3(7)
C(3)	0.791(1)	−0.419 4(8)	0.218 3(7)
C(4)	0.764(1)	−0.408 5(8)	0.305 4(5)
C(5)	1.033(1)	0.174 0(8)	0.470 8(6)
C(6)	0.927(1)	0.229 9(9)	0.498 3(7)
C(11)	0.524(1)	0.391(1)	0.036 9(9)
C(21)	0.407(1)	0.167(1)	−0.037 6(9)
C(31)	0.724(1)	−0.506(1)	0.175 9(8)
C(41)	0.833(1)	−0.480(1)	0.358 6(8)
C(51)	1.105(1)	0.131(1)	0.538 4(7)
C(61)	0.946(1)	0.343(1)	0.518 9(8)

the circular dichroism spectra of a chloroform solution: the Δε value at 665 nm decreased over 40 min from a positive to a negative peak until it reached a diastereomeric equilibrium.[5] A solution of the compound in acetonitrile was optically more stable, allowing crystals to be grown from this solution.

Crystallography.—Crystal data. $C_{12}H_{24}CrO_6P_3S_6$, *M* 601.60, orthorhombic, space group $P2_12_12_1$, $a = 11.699(1)$, $b = 12.738(2)$, $c = 16.827(2)$ Å, $U = 2507.6(6)$ Å^3 (by least-squares refinement on diffractometer angles for 24 automatically centred reflections with $30 < 2\theta < 40°$, $\lambda = 0.710\,69$ Å, $D_m = 1.60$ g cm^{-3}, $Z = 4$, $D_c = 1.593$ g cm^{-3}, $F(000) = 1\,236$, purple oblong plates, crystal dimensions (distance between faces) $0.03 \times 0.11 \times 0.38$ mm, $\mu(\text{Mo-}K_\alpha) = 11.69$ cm^{-1}.

Data collection. To obtain better reflection data sets, several data collections were carried out on different crystals using a sealed X-ray tube or a rotating anode from a molybdenum or copper target. The best data set was obtained using an AFC5R diffractometer with a rotating anode Mo-K_α source (60 kV, 150 mA) and only this experiment is described in this paper. Intensity data were collected as a primitive orthorhombic cell, although a C-centred cell was erroneously indicated by all the diffractometer data-collection software used. A 2θ—ω scan mode with ω scan width = 1.15 + 0.30 tanθ, ω scan speed 4° min^{-1} and for the weaker reflections a maximum of three scans were performed; graphite-monochromated Mo-K_α radiation; 5085 independent reflections measured ($1.5 \leqslant 2\theta \leqslant 65.0°$, $+hkl$, 23 °C), giving only 1537 with $I > 3\sigma(I)$ and 2 170 with $I > \sigma(I)$. No crystal decay was observed.

Structure determination. The space group was assigned to $P2_12_12_1$ from the systematic absences. The position of the Cr atom was located from the sharpened Patterson synthesis and the lighter atoms were gradually revealed from Fourier difference maps. Empirical absorption corrections (ψ scan) were applied: the minimum and average correction factors were 0.7327 and 0.9869, respectively. Due to strong correlations among the positional parameters of four molecules in the unit cell, the structure converged to a false mininum of $R = 0.112$ with non-positive definite thermal parameters for some lighter atoms and unacceptable bond lengths, *e.g.* C–C distances of 1.76 and 1.21 Å. The structure was eventually solved by shifting the starting co-ordinates for the refinement through careful checking of $|F_o| - |F_c|$ statistics. The structure was refined with full-matrix least squares based on *F* assuming anisotropic thermal parameters for the non-hydrogen atoms. Hydrogen atom positions were calculated assuming an ideal geometry, and they were included in the structure-factor calculations but not refined. The final *R* and *R′* factors were 0.0435 and 0.0492 respectively for the 1537 reflections with $I > 3\sigma(I)$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|)]^{\frac{1}{2}}$, and the weighting scheme was $w = 1/\sigma(F_o)^2$, with $\sigma(F_o)$ from counting statistics; goodness of fit = 1.05, number of parameters = 253, maximum shift/error = 0.01, and the highest peak in the final Fourier difference map was 0.361 e Å^{-3} around the Cr atom.

All the calculations were carried out on a MicroVAX II at Rigaku, Tokyo, using the computer programs TEXSAN[6] and ORTEP.[7] The f, f', and f'' data were taken from ref. 8.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Results and Discussion

Molecular Structure.—The final atomic parameters are listed in Table 1. Figure 1 presents the molecular structure with the numbering scheme employed. The molecule possesses a pseudo-D_3 symmetry. The CrS_6 co-ordination octahedron is distorted from a regular octahedron, with a 'bite' angle of 82.0° on average (see Table 2). The azimuthal projection of the intrachelate angle is 48.5°, much smaller than the 60° for a regular octahedron or 55° of five-membered [Co(en)$_3$], or 61.5° of six-membered [Cr(pd)$_3$] (pd = pentane-2,4-dionato anion). The four-membered chelate rings are almost planar with a mean deviation from the average plane of *ca.* 0.02 Å. The Cr–S–P angle is small (average 85.3°). The five-membered rings adopt a skew-boat conformation with a mean deviation of *ca.* 0.11 Å. All the methyl groups are equatorial to the five-membered ring planes.

The phosphorus atoms adopt a tetrahedral geometry; the four- and five-membered rings bonding to the same phosphorus atom are almost perpendicular to each other with dihedral angles of 90, 88 and 91° for the three pairs. Thus, the three inner rings and the three outer rings form a propeller of opposite handedness, as expected. The inner chelate and outer rings are tilted at an average angle of 58.8 and 32.1°, respectively, to the molecular C_3 axis. The three inner rings are almost perpendicular to each other with dihedral angles of 81, 85 and 87°, while the three outer rings are tilted only about 55° on average to each other. The absolute configuration of the molecule has been determined to be Λ(λλλ) based on the known absolute configuration of the ligand.

Crystal Packing.—There is one independent molecule per asymmetric unit, molecule I, and three other molecules in the unit cell, II—IV, are related to I by the 2_1 screw axes parallel to the crystal *b*, *c* and *a* axes, respectively (Figure 2). The chelate rings of the four molecules in the unit cell are almost parallel to each other, and the crystal-packing pattern clearly shows a pseudo-C-centring. This explains why all diffractometer software employed in the data acquisitions indicated a C-centred system, as well as the difficulty in refining the atomic co-ordinates.

The molecular C_3 axes lie in the *ac* plane forming an angle of 36.4° with the *a* axis. In addition, one of the three molecular C_2

Table 2. Bond distances (Å) and angles (°)

Cr–S(1)	2.424(3)	O(1)–C(1)	1.47(1)
Cr–S(2)	2.410(3)	O(2)–C(2)	1.46(1)
Cr–S(3)	2.426(3)	O(3)–C(3)	1.45(1)
Cr–S(4)	2.438(3)	O(4)–C(4)	1.45(1)
Cr–S(5)	2.423(4)	O(5)–C(5)	1.46(1)
Cr–S(6)	2.420(3)	O(6)–C(6)	1.47(1)
S(1)–P(1)	1.974(4)	C(1)–C(2)	1.50(2)
S(2)–P(1)	1.972(4)	C(3)–C(4)	1.51(1)
S(3)–P(2)	1.983(4)	C(5)–C(6)	1.51(1)
S(4)–P(2)	1.973(4)	C(1)–C(11)	1.51(1)
S(5)–P(3)	1.979(5)	C(2)–C(21)	1.52(2)
S(6)–P(3)	1.973(4)	C(3)–C(31)	1.53(2)
P(1)–O(1)	1.597(7)	C(4)–C(41)	1.51(1)
P(1)–O(2)	1.590(8)	C(5)–C(51)	1.52(1)
P(2)–O(3)	1.592(7)	C(6)–C(61)	1.50(2)
P(2)–O(4)	1.600(7)		
P(3)–O(5)	1.599(7)		
P(3)–O(6)	1.586(8)		
S(1)–Cr–S(2)	82.2(1)	O(1)–P(1)–O(2)	97.1(4)
S(3)–Cr–S(4)	81.7(1)	O(3)–P(2)–O(4)	97.6(4)
S(5)–Cr–S(6)	82.1(1)	O(5)–P(3)–O(6)	97.8(4)
S(1)–Cr–S(3)	91.1(1)	P(1)–O(1)–C(1)	111.8(6)
S(1)–Cr–S(5)	91.8(1)	P(1)–O(2)–C(2)	111.3(7)
S(1)–Cr–S(6)	94.5(1)	P(2)–O(3)–C(3)	110.7(6)
S(2)–Cr–S(3)	96.1(1)	P(2)–O(4)–C(4)	110.7(6)
S(2)–Cr–S(4)	91.3(1)	P(3)–O(5)–C(5)	109.8(6)
S(2)–Cr–S(6)	90.9(1)	P(3)–O(6)–C(6)	110.7(6)
S(3)–Cr–S(5)	91.4(1)	O(1)–C(1)–C(2)	104.2(8)
S(4)–Cr–S(5)	95.7(1)	O(2)–C(2)–C(1)	106(1)
S(4)–Cr–S(6)	93.4(1)	O(3)–C(3)–C(4)	106.0(9)
S(1)–Cr–S(4)	169.8(1)	O(4)–C(4)–C(3)	104.1(8)
S(2)–Cr–S(5)	170.4(1)	O(5)–C(5)–C(6)	105.3(8)
S(3)–Cr–S(6)	171.5(1)	O(6)–C(6)–C(5)	103.5(9)
Cr–S(1)–P(1)	85.1(1)	O(1)–C(1)–C(11)	109.3(8)
Cr–S(2)–P(1)	85.5(1)	O(2)–C(2)–C(21)	108(1)
Cr–S(3)–P(2)	85.2(1)	O(3)–C(3)–C(31)	109(1)
Cr–S(4)–P(2)	85.1(1)	O(4)–C(4)–C(41)	110(1)
Cr–S(5)–P(3)	85.2(1)	O(5)–C(5)–C(51)	109.2(9)
Cr–S(6)–P(3)	85.4(1)	O(6)–C(6)–C(61)	110(1)
S(1)–P(1)–S(2)	107.2(2)	C(2)–C(1)–C(11)	116.2(8)
S(3)–P(2)–S(4)	107.2(2)	C(1)–C(2)–C(21)	114(1)
S(5)–P(3)–S(6)	107.2(2)	C(4)–C(3)–C(31)	114(1)
S(1)–P(1)–O(1)	111.5(3)	C(3)–C(4)–C(41)	110(1)
S(2)–P(1)–O(2)	114.9(4)	C(6)–C(5)–C(51)	114(1)
S(3)–P(2)–O(3)	111.4(4)	C(5)–C(6)–C(61)	114(1)
S(4)–P(2)–O(4)	111.8(3)		
S(5)–P(3)–O(5)	112.0(3)		
S(6)–P(3)–O(6)	111.4(3)		

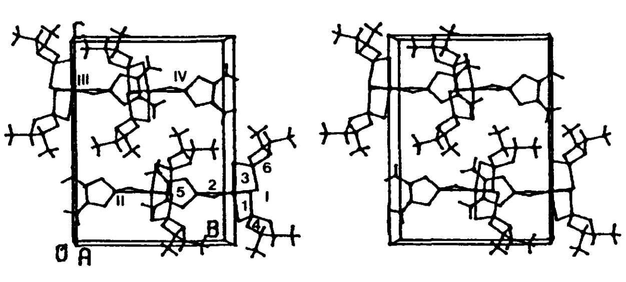

Figure 2. Stereoview of the unit cell along the crystal *a* axis, with molecular(I—IV) and plane(1—6) numbering schemes employed.

axes is parallel to the crystal *b* axis. Thus, the crystal structure can be regarded as being made up of two types of layers parallel to the *ab* plane. The two different layers consisting of an I–II pair or III–IV pair lie alternately on top of each other along the *c* axis. Table 3 summarizes the dihedral angles between the C_3 axes together with the distance between the central chromium atoms. Within each layer, molecules are related by a 2_1 screw axis parallel to the *b* axis. Because of the molecular orientation and location in the unit cell, the molecular C_3 and all three C_2 axes of I are parallel to the corresponding symmetry axes of II, as if the two molecules are related by translation along the $(a + b)/2$. Molecules belonging to different layers are related by 2_1 parallel to the *a* or *c* axis. In both cases, the dihedral angles between the C_3 axes are close to the tetrahedral angle or its supplement (Table 3).

Table 3. The observed angle between the molecular C_3 axes and the distance between the chromium atoms of nearest-neighbour molecules in the crystal structure

Molecule pair	Dihedral angle (°)	Cr . . . Cr distance (Å)
(*a*) Within a layer		
I . . . II	167.28	8.633
(*b*) Between layers		
I . . . III	107.17	8.416
I . . . IV	74.30	8.633

Chiral discrimination energies calculated based on a pairwise dispersion energy and van der Waals packing considerations have shown[3] that tris(chelate)metal 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. On the other hand, this type of D_3 complex packs economically in the plane orthogonal to the parallel molecular C_3 axes, only when adjacent molecules adopt opposite absolute configurations. This packing allows the contiguous chelate rings of racemic neighbours in the plane to assume a parallel mutual orientation. The contiguous chelate rings of two adjacent molecules with the same absolute configuration are tilted in opposite directions, resulting in poor crystal packing. Parallel orientation of the contiguous planes is achieved only when the two molecular C_3 axes become mutually orientated at the tetrahedral angle (109.5°) or its supplement (70.5°).

The above discussion applies to D_3 metal complexes involving a simple propeller system. We have previously compared crystal structures of optically active and racemic $[Cr(pd)_3]$.[4] In the racemic crystal structure[9] the C_3 axes are either parallel or tilted at a dihedral angle of 61.0° to each other. This type of crystal packing results in an interleaving of the chelate rings, which is not found in the molecular packing of the active crystal. In the active crystal[4] there are two independent molecules in the asymmetric unit, and the mutual orientations of the molecular C_3 axes are either close to parallel (3.7°) or to the supplement of the tetrahedral angle (75.3, 73.0 and 74.5°). Thus, all the chelate rings are almost parallel to each other, as in the case of Λ-$[Cr\{(-)bdtp\}_3]$.

The current complex possesses a compound propeller system in which the inner and outer propellers have opposite chirality. Mutual orientations of near-parallel and near-tetrahedral dihedral angles between the C_3 axes are observed in this compound, as is expected from theoretical considerations and as is found experimentally in simple propeller systems; however, the detailed packing modes are complicated. Table 4(*a*) summarizes the dihedral angles between planes in the unit cell. Planes 1—3 designate the inner chelate rings, while 4—6 designate the outer five-membered rings (Figure 2). All the molecules within a layer have a parallel mutual orientation. Between the layers, all the inner chelate-ring planes have parallel mutual orientation, whereas not all the outer rings do [Figure 2 and Table 4(*a*)]. Only the five-membered ring with the C_2 along the *b* axis (ring 5) is parallel to such rings of other molecules, and the other two

Table 4. Analysis of the crystal packing. Numbers 1—3 designate the inner rings and 4—6 the outer rings. Roman numbers are for symmetry operations*

(*a*) Dihedral angles (°) between planes in the unit cell

(*i*) Within a layer

		II					
		1	2	3	4	5	6
I	1	102	78	**13**	57	55	104
	2	78	**4**	90	133	88	128
	3	**13**	90	85	77	40	41
	4	57	133	77	41	50	**15**
	5	55	88	40	50	**4**	61
	6	104	128	41	**15**	61	69

(*ii*) Between layers

		III					
		1	2	3	4	5	6
I	1	**14**	95	94	80	49	36
	2	95	**168**	82	37	81	45
	3	94	82	**5**	51	45	94
	4	80	37	51	**94**	59	115
	5	49	81	45	59	**8**	64
	6	36	45	94	115	64	**86**

		IV					
		1	2	3	4	5	6
I	1	104	92	**10**	45	54	94
	2	92	**169**	85	39	81	42
	3	**10**	85	85	80	41	46
	4	44	39	81	108	56	**92**
	5	54	81	41	57	**8**	67
	6	94	42	46	**92**	67	125

(*b*) Distances (Å) between midpoints of nearest-neighbour planes

	Ring pair		Ring pair	
(*i*) Within a layer				
	I5 . . . II4	4.832	I5 . . . II6	5.706
	I5 . . . II6	5.661	I6 . . . II5	4.773
(*ii*) Between layers				
	I4 . . . III6	5.111	I3 . . . III4	5.830
	I6 . . . III1	5.543		

(*c*) Intermolecular distances (Å) (nearest neighbours)

	Atom pair			
(*i*) Within a layer				
	I—I	O(1) . . . C(31)	3.50(1)	56 501*
	I—I	C(11) . . . C(31)	3.56(1)	56 501
	I—II	O(3) . . . C(5)	3.51(1)	74 502
	I—II	O(3) . . . O(5)	3.56(1)	74 502
	I—II	O(5) . . . C(3)	3.46(1)	74 502
(*ii*) Between layers				
	I—III	O(2) . . . C(51)	3.35(1)	65 403
	I—III	C(11) . . . C(61)	3.42(1)	66 403
	I—III	O(5) . . . C(21)	3.51(1)	65 503
	I—IV	O(6) . . . C(51)	3.46(1)	45 604

* These symmetry codes are those used in the ORTEP program.[7] The last digits in (*c*) as well as I—IV in (*a*) and (*b*) indicate symmetry operation numbers: 1 or I x, y, z; 2 or II $-x, \frac{1}{2} + y, \frac{1}{2} - z$; 3 or III $\frac{1}{2} - x, -y, \frac{1}{2} + z$; 4 or IV $\frac{1}{2} + x, \frac{1}{2} - y, -z$.

rings (4 and 6) take almost perpendicular mutual orientations to the corresponding rings [Table 4(*a*)].

Table 4(*b*) gives the distance between the midpoint of nearest-neighbour planes, and Table 4(*c*) lists the intermolecular interatomic distances less than 3.6 Å. The closest interatomic contacts are found between molecules I and III (or II and IV) belonging to different layers: the methyl groups are in close contact with atoms of the outer rings of the other molecules. In addition to close interactions between outer rings within a layer or between layers [Tables 4(*b*) and (*c*)], an inner ring of one molecule is close to an outer ring of the other molecule and *vice versa* [I3 ... III4 and I6 ... III1, see Table 4(*b*)]. The inner and outer rings each form a propeller system of opposite handedness. If the molecules were to adopt one propeller system, the two chelate rings in close contact would be tilted in opposite directions, and hence this type of packing would not be so efficient. The dihedral angles between the contacting rings are 36 and 51°. The mutual orientation affords a nice interleaving of ring planes.

In the current structure there are also close contacts between the S atoms. The S ... S distance of 3.668 Å along the *c* axis is comparable to the corresponding distances of 3.700 and 3.634 Å reported as close contacts for dinaphtho[2,1-*c*:1′,2′-*e*]dithin[10] and dibenzyl disulphide,[11] respectively. Two other S ... S distances in the crystal structure are 3.834 and 3.847 Å.

In conclusion, the system described here is ideal for studying chiral discriminations/recognitions and packing in the crystalline state as the complex is neutral and the crystal is devoid of solvent molecules. The crystal-packing mode appears to be governed by the interleaving of ligands through inner–outer ring contacts as well as by parallel ring orientations found in many crystal structures of D_3 tris(chelate)metal complexes. Comparison of the structure with that of the racemic crystal may be revealing. In the case of ionic compounds, electrostatic considerations must be taken into account. A crystal-packing comparison of ionic chiral D_3 tris(chelate)metal complexes with hydrogen-bonding capability will be published elsewhere.

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