

Dipyridinium dichromate: an achiral compound forming chiral crystals

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The title compound, $(C_5H_6N)_2[Cr_2O_7]$, crystallizes in one of the Sohncke space groups, *viz.* $P2_12_12_1$. Crystallization of dipyridinium dichromate is thus an example of spontaneous formation of a chiral crystal structure from achiral molecules. The dichromate anion adopts a virtually eclipsed achiral conformation, and the crystal structure is held together primarily by $N-H\cdots O$ and $C-H\cdots O$ interactions. The possibility of using dipyridinium dichromate as a reagent in enantioselective synthesis is discussed.

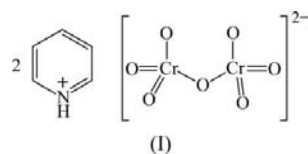
Comment

Spontaneous resolution is the phenomenon where the two enantiomers in a racemic solution crystallize in separate chiral crystals (Elieil *et al.*, 1994). Racemic solutions of stereochemically inert compounds will yield a racemic conglomerate, which is a 1:1 mixture of the two enantiomorphous crystals. On the other hand, a stereochemically labile substance may undergo total spontaneous resolution, also known as crystallization-induced asymmetric transformation (Jacques *et al.*, 1984). This means that the whole crystal batch may grow from a single nucleus, and the whole batch will be enantiomerically pure. The requirement is, of course, that the two enantiomers will interconvert rapidly in solution, so that the whole amount of solute is transformed into one single enantiomer upon crystallization.

Enantiomerically pure crystals belong to one of the 65 Sohncke space groups (Flack, 2003). What if an achiral substance crystallizes in such a space group? Crystallization of an achiral substance in a Sohncke space group will give chiral crystals, where the molecules or ions will display a chiral packing. Well known examples include α -quartz, magnesium sulfate heptahydrate, strontium formate and sodium chlorate (Groth, 1921). The crystals may appear as two enantiomorphs, and crystallization-induced asymmetric transformation is possible (Kondepudi *et al.*, 1990; McBride & Carter, 1991; Pagni & Compton, 2002). It has been shown that DL-alanine hydrochloride may be enantioselectively adsorbed on quartz crystals (Bonner & Kavasmaneck, 1976), and both quartz (Soai *et al.*, 1999) and sodium chlorate (Sato *et al.*, 2000)

induce high enantioselectivity in Soai's asymmetric autocatalytic reaction (Soai *et al.*, 1995).

Crystallization-induced asymmetric transformation may be regarded as a means of achieving absolute asymmetric synthesis, *i.e.* the creation of optically active substances from achiral or racemic starting materials only (Feringa & van Delden, 1999). Over the years, we have studied the total spontaneous resolution of stereochemically labile chemical reagents (Vestergren *et al.*, 2000, 2003; Håkansson *et al.*, 1999) and potential substrates (Johansson & Håkansson, 2005; Lennartson, Salo & Håkansson, 2005; Andersson *et al.*, 1986; Lennartson *et al.*, 2007). A stereochemically labile oxidizing agent would be attractive, since in principle it would be possible to convert, for example, a prochiral sulfide to a chiral sulfoxide, or to partially degrade a chiral (racemic) alcohol to an achiral carbonyl compound leaving an enantiomeric excess in the remaining alcohol. For such a reaction to be successful, the chirality of the crystal structure must induce an enantiomeric excess in the product, and the reaction must be carried out under conditions where the reagent does not dissolve, since dissolution would destroy the chirality of the crystal structure. In the search for such substances, we found that a commercial sample of bis(pyridinium) dichromate, known as PDC to organic chemists, was made up by a phase, (I), crystallizing in the Sohncke space group $P2_12_12_1$.



PDC is a useful oxidizing agent in organic synthesis. A suspension of PDC in methylene chloride is a mild oxidizing agent that converts both saturated and unsaturated alcohols to aldehydes and ketones (Corey & Schmidt, 1979). The reaction is accelerated by the presence of molecular sieves (Herscovici & Antonakis, 1980), and the oxidation of alcohols can also be carried out catalytically using bis(trimethylsilyl) peroxide as bulk-oxidant (Kanemoto *et al.*, 1988). A solution of an aliphatic aldehyde and methanol in dry dimethylformamide gives a methyl ester (O'Connor & Just, 1987), cyclic alkenes give α -iodo-ketones when treated with PDC and iodine in dry methylene chloride (D'Ascoli *et al.*, 1980), and the same group found that trisubstituted alkenes can be transformed into iodohydrines or, with a longer reaction time, to epoxides (Antonioletti *et al.*, 1983). Cyanohydrines give carboxylic acids with PDC in dimethylformamide (Corey & Schmidt, 1980), and Brown *et al.* (1992) have converted organoboranes to carbonyl compounds using PDC. Today, chemical supplying companies such as Sigma-Aldrich or Acros Organics also offer bis(pyridinium) dichromate on a silica support.

Surprisingly, a search of the Cambridge Structural Database (CSD, Version 5.30, update of November 2008; Allen 2002) indicated that no full crystal structure determination of (I) has been reported to date. Two phases of bis(pyridinium) dichromate are reported (Gili, 1984), but they do not corre-

spond to compound (I). Both appear to be triclinic but no space group is reported. In addition, only a limited number of dichromates displaying substituted pyridinium counter-ions are found in the CSD. These include bis(5-nitropyridinium) dichromate (Pecaut & Masse, 1993), bis(2,6-dimethylpyridinium) dichromate (Jin *et al.*, 2006), bis(quinolinium) dichromate (Sundar *et al.*, 2003), and bis(2,4'-bipyridinium) dichromate, bis(2,2'-dipyridylaminium) dichromate and bis(4,4'-dipyridinium) dichromate (Martin-Zarza *et al.*, 1995). Among the previously reported substituted pyridinium dichromates, bis(2,6-dimethylpyridinium) dichromate also crystallizes in a Sohncke space group with a low Flack parameter (Flack, 1983; Bernardinelli & Flack, 1985).

The molecular structure of (I) is unremarkable (Fig. 1). The coordination geometries around atoms Cr1 and Cr2 are distorted tetrahedral, and the dichromate ion adopts an eclipsed conformation. This arrangement is similar to that in bis(4,4'-dipyridinium) dichromate, but different from that in bis(2,6-dimethylpyridinium) dichromate, where the dichromate ion adopts a virtually staggered conformation. The assembly of the crystal structure appears to rely largely on N—H...O and C—H...O interactions between anions and cations (Table 1). This was anticipated by Gili (1984) on the basis of ^1H NMR and IR spectroscopy. Each anion forms short $D\text{—H}\cdots A$ contacts with surrounding pyridinium cations, and the interaction pattern of (I) is rather complex. Atom O1 forms two contacts, to atoms H1($-x + \frac{3}{2}, -y + 2, z - \frac{1}{2}$) and H7($-x + \frac{3}{2}, -y + 2, z + \frac{1}{2}$). Atom O2 forms two short contacts to atoms H12($-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$) and H4($-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$), although the $D\text{—H}\cdots A$ angles are small and both H atoms are involved in other interactions. Atom O3 forms two short contacts, to H9($-x + \frac{1}{2}, -y + 2, z + \frac{1}{2}$) and to H6($-x + \frac{3}{2}, -y + 2, z + \frac{1}{2}$). Atom O4, the O atom bridging atoms Cr1 and Cr2, forms a short contact to atom H8($-x + \frac{1}{2}, -y + 2, z + \frac{1}{2}$) and a short contact to atom H11($-x + \frac{1}{2}, -y + 2, z - \frac{1}{2}$). Thus, atoms O3 and O4 are interconnected by two adjacent H atoms

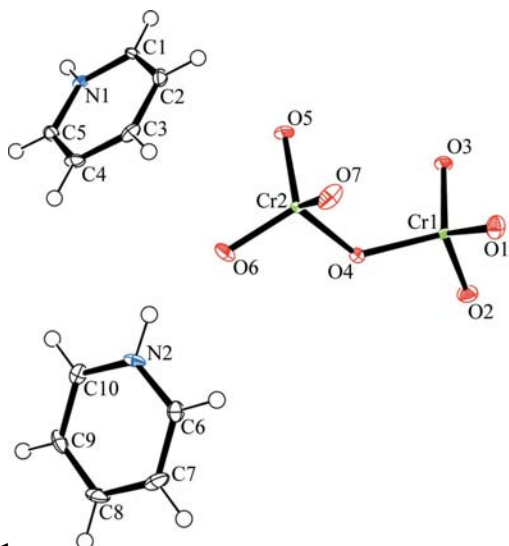


Figure 1

The molecular structure of (I), showing the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are included with an arbitrary radii.

in one pyridinium cation. Atoms O1 and O3 are interconnected in a similar manner. Atom O5 forms a short contact with atom H5($x + 1, y, z$), the same pyridinium cation forming a short contact with atom O7 through H4($x + 1, y, z$). Atom O7 forms an additional contact with atom H10($x + 1, y, z$). Atom O6 forms a short contact with H12, the only short contact within the asymmetric unit. All the H atoms appear to be involved in hydrogen bonding except for atoms H2 and H3. Atom H12 connects adjacent cations giving rise to zigzag ribbons extended in the [010] direction. Adjacent ribbons intercalate, resulting in a layered structure in which alternating layers of dichromate anions and pyridinium cations are stacked along c (Fig. 2). On inspecting the crystal structure it is not obvious from where the chirality originates, the anion being locked in an achiral conformation; the chirality is therefore to be traced to the orientation of the ions in the unit cell. It therefore appears very unlikely that a reaction between, for example, 1-phenylethanol and (I) would give rise to any measurable enantioselectivity.

It is not trivial to determine if all the crystals in a batch of (I) are of the same enantiomorph or not; such a determination must be carried out in the solid state, and well known methods such as polarimetry are of no use. There are in principle two ways this could be carried out: either by solid-state circular dichroism (CD) spectroscopy or by single-crystal X-ray diffraction on a large number of crystals (distinction between enantiomorphs by observation in polarized light is only possible for crystals of the cubic system). We have developed a method for measuring enantiomeric excess of stereochemically labile molecules by means of solid-state CD spectroscopy (Lennartson, Vestergren & Håkansson, 2005): the value of the solid-state CD of an enantiopure single crystal was found to be proportional to the mass. Enantiomorph purity can therefore be measured by comparing the CD of a microcrystalline sample with that of a single crystal. In the case of (I), however, we were not able to observe any CD, not even for single crystals. The Flack parameter of the analysed crystal is low, 0.01 (2), and there was no indication of twinning-

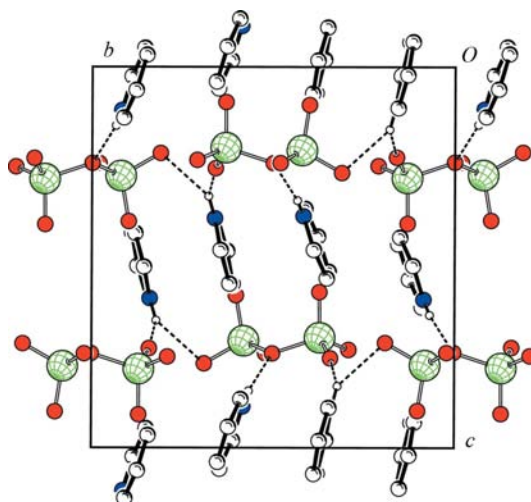


Figure 2

A view, along the a axis, of the crystal structure of (I).

by-inversion in crystals of (I). It is therefore not unlikely that slow crystallization of (I) would afford exclusive crystallization of one enantiomorph only.

Experimental

A crystal of the title compound was carefully selected from a commercial sample of dipyridinium dichromate (Fluka).

Crystal data

$(C_5H_6N)_2[Cr_2O_7]$	$V = 1410.5 (4) \text{ \AA}^3$
$M_r = 376.22$	$Z = 4$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 8.2797 (17) \text{ \AA}$	$\mu = 1.57 \text{ mm}^{-1}$
$b = 12.741 (2) \text{ \AA}$	$T = 100 \text{ K}$
$c = 13.371 (2) \text{ \AA}$	$0.3 \times 0.2 \times 0.1 \text{ mm}$

Data collection

Rigaku R-AXIS IIC image-plate system diffractometer	9462 measured reflections
Absorption correction: multi-scan (CrystalClear; Rigaku, 2000)	2505 independent reflections
$T_{\min} = 0.647$, $T_{\max} = 0.850$	2441 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.033$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$	$\Delta\rho_{\text{max}} = 0.29 \text{ e \AA}^{-3}$
$wR(F^2) = 0.063$	$\Delta\rho_{\text{min}} = -0.34 \text{ e \AA}^{-3}$
$S = 1.06$	Absolute structure: Flack (1983),
2505 reflections	1055 Friedel pairs
198 parameters	Flack parameter: 0.01 (2)
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H11\cdots O4^i$	0.74 (3)	1.97 (3)	2.705 (3)	171 (3)
$N2-H12\cdots O2^{ii}$	0.94 (4)	2.45 (4)	3.013 (3)	118 (3)
$N2-H12\cdots O6$	0.94 (4)	1.87 (4)	2.704 (3)	147 (3)
$C1-H1\cdots O1^{iii}$	0.93	2.39	3.094 (3)	132
$C4-H4\cdots O7^{iv}$	0.93	2.66	3.512 (4)	153
$C4-H4\cdots O2^{ii}$	0.93	2.61	3.182 (3)	120
$C5-H5\cdots O5^{iv}$	0.93	2.36	3.210 (3)	153
$C6-H6\cdots O3^v$	0.93	2.53	3.244 (3)	133
$C7-H7\cdots O1^v$	0.93	2.57	3.451 (4)	159
$C8-H8\cdots O4^{vi}$	0.93	2.57	3.459 (4)	160
$C9-H9\cdots O3^{vi}$	0.93	2.42	3.190 (3)	140
$C10-H10\cdots O7^{iv}$	0.93	2.30	3.169 (3)	156

Symmetry codes: (i) $-x + \frac{1}{2}, -y + 2, z + \frac{1}{2}$; (ii) $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$; (iii) $-x + \frac{3}{2}, -y + 2, z + \frac{1}{2}$; (iv) $x - 1, y, z$; (v) $-x + \frac{3}{2}, -y + 2, z - \frac{1}{2}$; (vi) $-x + \frac{1}{2}, -y + 2, z - \frac{1}{2}$.

Atoms H11 and H12 were located in a difference Fourier map and freely refined. The C-bound H atoms were included in calculated positions ($C-H = 0.93 \text{ \AA}$) and treated as riding [$U_{\text{iso}}(H) = 1.2U_{\text{iso}}(C)$].

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLUTON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SU3032). Services for accessing these data are described at the back of the journal.

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