metal-organic compounds

Poly[(*μ*₆-*rac*-*cis*-cyclohexane-1,2-dicarboxylato)strontium]

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In the title layered coordination polymer, $[Sr(C_8H_{10}O_4)]_n$, the strontium ion adopts a distorted square-antiprismatic SrO_8 geometry, arising from its coordination by six different *cis*-cyclohexane-1,2-dicarboxylate dianions (two bidentate and four monodentate). Within the dianion, the cyclohexane ring adopts a chair conformation and the dihedral angle between the planes of the $–CO_2^-$ groups is 80.4 (6)°. The polyhedral linkage pattern leads to (100) sheets in the crystal in which the SrO_8 groups share triangular faces and edges in which the Sr···Sr topological connectivity is a 6^3 net. The crystal studied was a nonmerohedral twin, with the components related by a 180° rotation about [100].

Comment

Cyclohexane-1,2-dicarboxylic acid (H₂chdca) is an interesting candidate for combining with metal ions in its doubly deprotonated form (chdca) to generate new types of coordination polymers containing an extended network of metal–oxygen links. The stereochemistry of H₂chdca requires careful consideration: like other 1,2-disubstituted cyclohexanes, it can exist as *cis* and *trans* isomers, both of which contain two stereogenic centres and are chiral as individual molecules. Alternate names for these forms are axial–equatorial (ae) and an equilibrating mixture of axial–axial/equatorial–equatorial (aa/ee), respectively (Eliel & Wilen, 1994; Thirumurugan *et al.*, 2006). The *cis* form is racemic [or *meso* according to a group theoretical treatment (Leonard *et al.*, 1975)] in solution because the two rapidly equilibrating chair forms are enantiomers of each other (one *RS* and one *SR*), but a spontaneous resolution into an enantiomorphous (chiral) crystal containing only the *RS* (or *SR*) form is possible, although the bulk material will of course contain equal numbers of the two enantiomorphs.

Thus, in principle, there are four stereochemical possibilities (homochiral-*cis*, racemic-*cis*, homochiral-*trans* and racemic-*trans*) for an individual single crystal containing chdca in combination with a particular metal ion. However, not all combinations may be realizable in practice because unex-

pected racemizations and isomerizations can occur under the mild hydrothermal conditions normally used to synthesize the target phases (Lee *et al.*, 2006; Zheng, Xue, Zheng *et al.*, 2008).


(I)
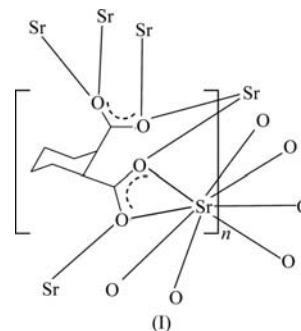
The homochiral-*trans* and racemic-*trans* forms of Zn(chdca) have been structurally characterized (Bailey *et al.*, 2008) and their stabilities compared: both thermochemical measurements and calculations indicate that the racemic form is more stable. Zheng, Xue, Tong *et al.* (2008) prepared a series of coordination polymers with unusual magnetic properties containing divalent transition metal ions and *cis* and *trans* chdca dianions. Larger divalent cations such as Cd^{2+} (Thirumurugan *et al.*, 2006) and Pb^{2+} (Rao *et al.*, 2007) lead to different types of networks: Cd(chdca) is a layered structure containing distorted CdO_6 octahedra sharing edges and corners, whereas the layers in Pb(chdca) are built up from irregular PbO_8 building blocks, also sharing edges and faces. Using the trivalent In^{3+} cation led to In(OH)(chdca), a layered structure (Kim *et al.*, 2010) with possible inter-layer porosity.

The title compound, Sr(chdca), (I) (Fig. 1), is a new coordination polymer that complements the phases noted above. The cyclohexane ring of the anion in (I) adopts its typical chair conformation with normal bond lengths (Allen *et al.*, 1987) and angles similar to those seen in related compounds (Benedetti *et al.*, 1970; Lee *et al.*, 2006). The C7—C1—C2—C8 torsion angle of 57.5 (7)° confirms the presence of the *cis* isomer (also known as the axial–equatorial form; see Thirumurugan *et al.*, 2006). As noted above, the dianion contains two stereogenic centres: in the arbitrarily chosen asymmetric
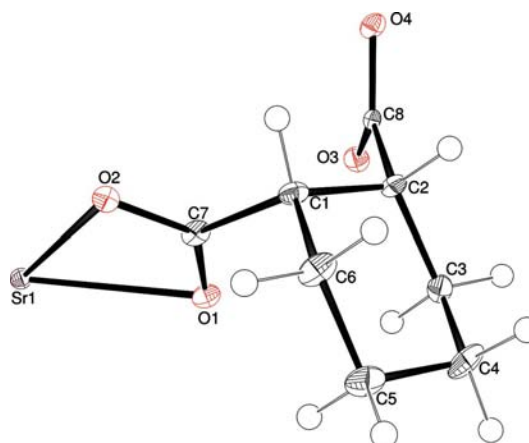
Figure 1
A view of the asymmetric unit of (I), with displacement ellipsoids drawn at the 50% probability level.
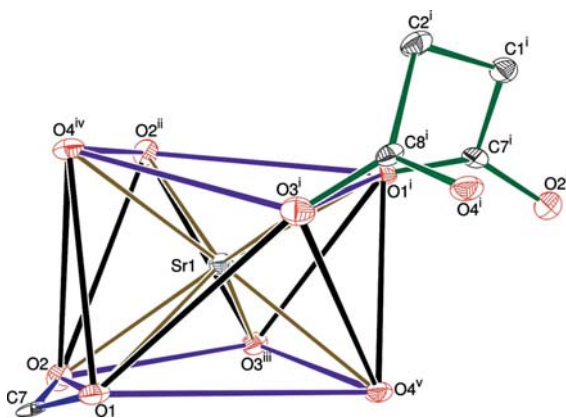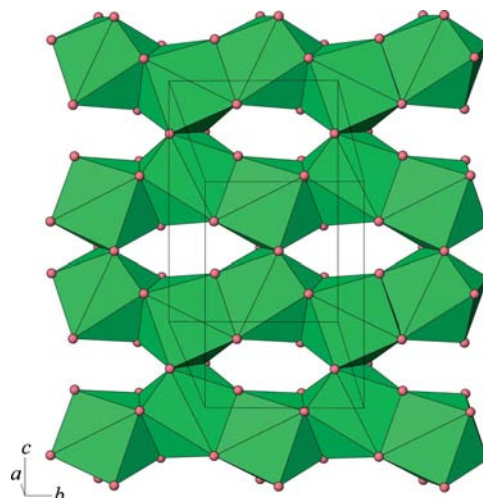
Figure 2
A fragment of (I), showing the coordination polyhedron of the strontium ion. O1 and O2 are part of the chelating carboxylate group (*A*) and O1^{i} and O3^{i} are part of the molecule (*B*) that bonds from different carboxylate groups. (In the electronic version of the paper, the following colour key applies: Sr—O bonds are gold, O···O contacts defining the square faces of the antiprism are fuscia, bonds within molecule *A* are blue and bonds within molecule *B* are forest green.) [Symmetry codes: (i) $1 - x$, $\frac{1}{2} + y, \frac{1}{2} - z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $x, 1 + y, z$; (iv) $1 - x, -y, 1 - z$; (v) $x, \frac{1}{2} - y, z - \frac{1}{2}$.]

molecule, C1 has *S* configuration and C2 *R*, but crystal symmetry generates a racemic mixture, in conformity with the starting material, *i.e.* spontaneous resolution on crystallization has not occurred in (I). The dihedral angle between the carboxylate planes (C7/O1/O2 and C8/O3/O4) is 80.4 (6)° and the C—O bond lengths (Table 1) indicate delocalization of both of the carboxylate negative charges. However, the bonding modes of the C7/O1/O2 and C8/O3/O4 carboxylate groups are distinctly different: O1 and O2 are bidentate to the Sr^{2+} ion in the asymmetric unit and monodentate to one other metal ion, whereas O3 and O4 are μ_2-bridging between strontium ions. The fact that O1 and O3 both link to Sr1^{vi} [symmetry code: (vi) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$] means that each dianion links to six different cations.

These anion bonding modes result in the strontium cation in (I) (Fig. 2) being bonded to eight O atoms from six distinct anions (one *O*,*O'*-bidentate from one carboxylate group, one *O*,*O'*-bidentate from two carboxylate groups and four monodentate). It is notable that the Sr—O bonds to the chelating carboxylate group are the two longest. Overall, the cation adopts a distorted SrO$_8$ square-antiprismatic geometry: the mean Sr—O separation is 2.57 (2) Å and the dihedral angle between the mean planes of O1/O2/O3^{iii}/O4^{v} and O1^{i}/O2^{ii}/O3^{i}/O4^{iv} is 6.25 (13)° (the symmetry codes are as in Fig. 2).

In the crystal, the SrO$_8$ polyhedra share triangular faces (*via* O1, O3^{i} and O4^{iv}) to generate undulating columns propagating along [010]. The columns share polyhedral edges (O2 and O2^{ii}) in the *c* direction to generate infinite sheets (Fig. 3) propagating along (100), with the pendant cyclohexane rings projecting into the inter-sheet regions (Fig. 4). The topological connectivity of the strontium nodes is a honeycomb 6^3 grid (O'Keeffe & Hyde, 1996).

The structure of (I) has some similarities to that of Pb(chdca) (Rao *et al.*, 2007), which also features polyhedral

Figure 3
Side-on polyhedral view of the Sr/O network in (I), showing the edge- and face-sharing connectivity, with all the C and H atoms omitted for clarity.
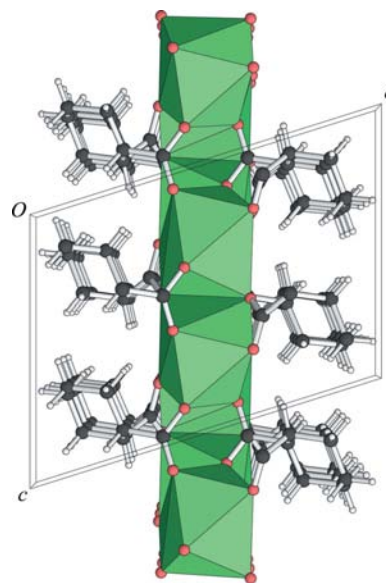
Figure 4
View down [010] of a polyhedral sheet in (I), showing the organic residues projecting into the inter-layer regions.

sheets based on a 6^3 grid. However, the ligand bonding modes (two *O*,*O'*-bidentate from the same carboxylate group and four monodentate) and metal geometries are different, perhaps in part due to the stereochemical activity of the Pb^{2+} lone pair of electrons.

Experimental

SrCO$_3$ (1 mmol, 1.476 g) and racemic *cis*-cyclohexane-1,2-dicarboxylic acid (1 mmol, 1.721 g) were added to water (20 ml) in a plastic bottle. The bottle was sealed and shaken well to generate a milky suspension and placed in a 353 K oven for 5 d. The bottle was cooled, and colourless blades and chunks of (I) were recovered by vacuum filtration and washed with water and acetone.

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Crystal data

$[Sr(C_8H_{10}O_4)]$
$M_r = 257.78$
Monoclinic, $P2_1/c$
$a = 13.3937$ (4) Å
$b = 7.0389$ (2) Å
$c = 9.9710$ (2) Å
$\beta = 107.555$ (2)°

$V = 896.26$ (4) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 5.99$ mm^{-1}
$T = 120$ K
$0.45 \times 0.10 \times 0.03$ mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan
  (*TWINABS*; Bruker, 2003)
  $T_{min} = 0.173$, $T_{max} = 0.841$

2054 measured reflections
2054 independent reflections
1856 reflections with $I > 2\sigma(I)$
$R_{int} = 0.000$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.162$
$S = 1.07$
2054 reflections

119 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 1.26$ e Å^{-3}
$\Delta\rho_{min} = -2.29$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Sr1—O3^i	2.506 (5)	Sr1—O2	2.631 (5)
Sr1—O1^i	2.518 (4)	Sr1—O1	2.656 (4)
Sr1—O2^{ii}	2.523 (5)	C7—O2	1.260 (8)
Sr1—O3^{iii}	2.550 (5)	C7—O1	1.266 (8)
Sr1—O4^{iv}	2.625 (5)	C8—O4	1.268 (8)
Sr1—O4^v	2.582 (4)	C8—O3	1.270 (8)

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

The crystal studied was a nonmerohedral twin [domain ratio is 0.59 (1):0.41 (1)], with the twin components related by a 180° rotation about the direct vector [100]. The reflection data were processed with *EVALCCD* (Duisenberg *et al.*, 2003) and *TWINABS* (Bruker, 2003) to generate a list of $|F^2|$ values with twin-contributor indicators (*SHELXL* format HKLF 5). For more information on data reduction and the modelling of nonmerohedrally twinned crystals, see Müller *et al.* (2006). The H atoms were placed in calculated positions (C—H = 0.99–1.00 Å) and refined as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997), *SCALEPACK*, *EVALCCD* (Duisenberg *et al.*, 2003) and *SORTAV* (Blessing, 1995); program(s)

used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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