

## A novel two-dimensional layered framework built of strontium(II) with 4-nitrobenzene-1,3-dicarboxylic acid

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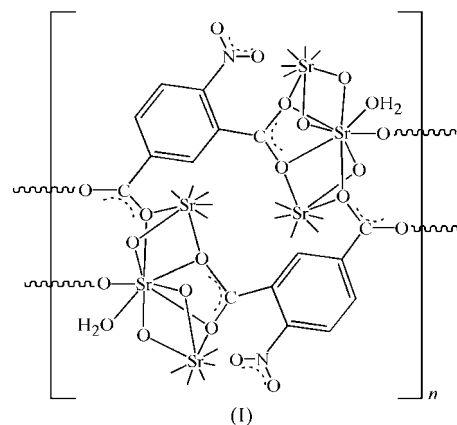
In poly[[aquastrontium(II)]- $\mu_6$ -4-nitrobenzene-1,3-dicarboxylato- $\kappa^7$ O<sup>1</sup>:O<sup>2</sup>:O<sup>2</sup>:O<sup>3</sup>:O<sup>3</sup>:O<sup>4</sup>:O<sup>4</sup>], [Sr(C<sub>8</sub>H<sub>3</sub>NO<sub>6</sub>)(H<sub>2</sub>O)]<sub>n</sub>, the Sr<sup>II</sup> ion displays a distorted bicapped triangular prismatic configuration, defined by seven carboxyl O atoms from six symmetry-related ligands and one water molecule. The ligand molecules connect the Sr<sup>II</sup> ions into a two-dimensional layered framework in the *ac* plane, with close O...O contacts between the nitro groups and with each nitro group providing one acceptor O atom for a weak intermolecular C—H...O hydrogen bond.

### Comment

In recent years, much interest has been focused on the design and synthesis of coordination polymers due to their intriguing architectures and favourable properties (Biradha & Fujita, 2002; Lee & Lin, 2002; Lin *et al.*, 2000; Moulton & Zaworotko, 2001; Sun *et al.*, 2002; Tominaga *et al.*, 2002). The selected ligand is an important factor that greatly influences the structure of the coordination polymer and the functionality of the complex formed. 4-Nitrobenzene-1,3-dicarboxylic acid can act as a multifunctional organic ligand *via* various coordination modes to metal ions, utilizing completely or partially deprotonated sites, and can provide suitable hydrogen-bond acceptors and donors. In addition, the noncoordinated -NO<sub>2</sub> functional group may assist in the creation of supramolecular assemblies through the simultaneous formation of dative and noncovalent bonds (Pedireddi & Varughese, 2004; Luo *et al.*, 2003). The structures of alkali earth metal complexes have been explored less than the extensively investigated transition metal complexes. We report here a novel Sr<sup>II</sup> coordination polymer, [Sr(NO<sub>2</sub>-BDC)(H<sub>2</sub>O)]<sub>n</sub> (NO<sub>2</sub>-H<sub>2</sub>BDC is 4-nitrobenzene-1,3-dicarboxylic acid), (I).

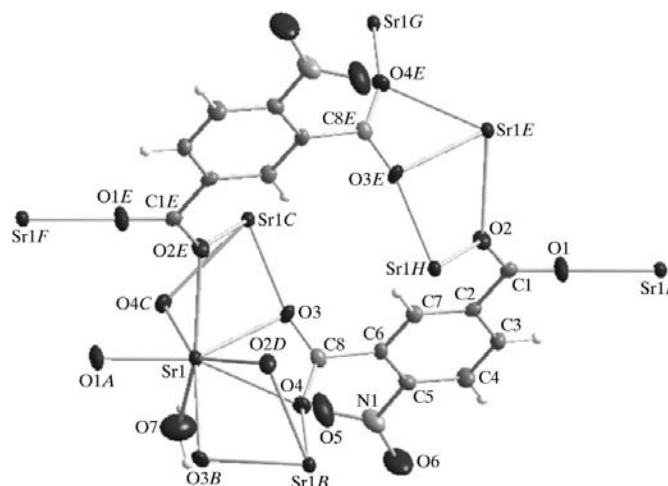
The asymmetric unit of (I) consists of one Sr<sup>II</sup> ion, one NO<sub>2</sub>-BDC ligand and one coordinated water molecule (Fig. 1). Each Sr<sup>II</sup> ion is eight-coordinate *via* seven O atoms of six symmetry-related NO<sub>2</sub>-BDC ligands (see the caption to Fig. 1 for the designations of these ligands) and one O atom of a

water molecule. The coordination environment of the Sr<sup>II</sup> ion can be described as a distorted bicapped triangular prism. The dihedral angle between the two basal planes (O<sub>2</sub>D/O<sub>3</sub>/O<sub>4</sub> and O<sub>1</sub>A/O<sub>4</sub>C/O<sub>7</sub>) is 18.38 (15)°, and the vertical distances



between the two capping atoms, O<sub>2</sub>E and O<sub>3</sub>B, and their side planes O<sub>1</sub>A/O<sub>2</sub>D/O<sub>3</sub>/O<sub>4</sub>C and O<sub>1</sub>A/O<sub>2</sub>D/O<sub>4</sub>/O<sub>7</sub> are 2.061 (3) and 1.847 (3) Å, respectively. The Sr—O bond distances fall in the range 2.458 (3)–2.783 (3) Å (mean 2.600 Å; Table 1) and are all within the range of those observed for other eight-coordinated Sr<sup>II</sup> complexes with O-donor ligands (Davies *et al.*, 2001; Deng *et al.*, 2005; Marchetti *et al.*, 2006; Stahl *et al.*, 2006).

In (I), the O<sub>1</sub>/C<sub>1</sub>/O<sub>2</sub> group of NO<sub>2</sub>-BDC adopts a tridentate bridging coordination mode to bind three Sr<sup>II</sup> ions, while the O<sub>3</sub>/C<sub>8</sub>/O<sub>4</sub> group coordinates to one Sr<sup>II</sup> ion in a bidentate chelate fashion and further bridges another two Sr<sup>II</sup> ions through two three-coordinating O atoms (Fig. 1). The O<sub>1</sub>/C<sub>1</sub>/O<sub>2</sub> group of NO<sub>2</sub>-BDC is nearly coplanar with the benzene ring, with an interplanar angle of 4.3 (5)°, while the O<sub>3</sub>/C<sub>8</sub>/O<sub>4</sub> group shows a large distortion from planarity with the benzene



**Figure 1**

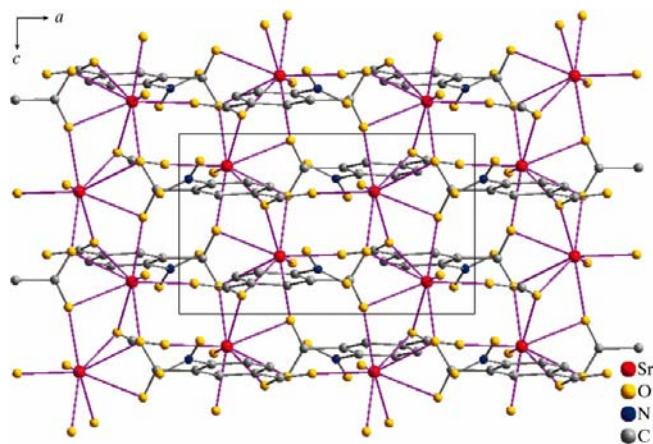
A view of the coordination of the Sr<sup>II</sup> atom in (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H-atom radii are arbitrary. [Symmetry codes: (A)  $-1 + x, y, z$ ; (B)  $\frac{1}{2} - x, y, \frac{1}{2} + z$ ; (C)  $\frac{1}{2} - x, y, -\frac{1}{2} + z$ ; (D)  $-\frac{1}{2} + x, 1 - y, \frac{1}{2} - z$ ; (E)  $1 - x, 1 - y, -z$ ; (F)  $-x, 1 - y, -z$ ; (G)  $\frac{1}{2} + x, 1 - y, -\frac{1}{2} - z$ ; (H)  $\frac{1}{2} + x, 1 - y, \frac{1}{2} - z$ ; (I)  $1 + x, y, z$ .]

ring, with a dihedral angle of  $62.5 (5)^\circ$ . The identical C—O bond distances [ $1.249 (5) \text{ \AA}$ ] in O3/C8/O4 are different from those in the O1/C1/O2 group (Table 1), as might be expected from the different coordination modes of the two carboxylate groups. However, the average carboxylate C—O bond distance of  $1.250 (5) \text{ \AA}$  is identical to that in the complex  $[\text{La}_2(\text{HL})_2(\text{L})_2(\text{H}_2\text{O})_6]\cdot 2\text{H}_2\text{O}$  [ $1.256 (4) \text{ \AA}$ ;  $\text{H}_2\text{L}$  is 3-nitrobenzene-1,2-dicarboxylic acid; Xiong & Qi, 2007] and that in  $[\text{Mn}(\text{NO}_2\text{-HBDC})_2(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$  [ $1.254 (3) \text{ \AA}$ ; Xiong *et al.*, 2007].

Interestingly, the  $\text{Sr}^{\text{II}}$  ions are bridged by three O atoms of carboxylate groups (O3, O2E and O4C) in a ‘three-bladed propeller’ mode to form a one-dimensional chain with Sr—O—Sr connectivity parallel to the  $c$  axis of the unit cell with similar O—Sr—O angles (Table 1). This mode has been reported in the complex strontium bis- $N,N$ -di(isopropyl)-aminoethylamino-2-penten-4-onate (Sergej *et al.*, 2005), but there the Sr—O—Sr connectivity is limited to trimer units.

The O1/C1/O2 groups of  $\text{NO}_2$ -BDC, acting as T-shaped units, link the  $\text{Sr}^{\text{II}}$  ions to form a one-dimensional chain with Sr—O—C—O—Sr connectivity parallel to the  $a$  axis of the unit cell. As a result, a two-dimensional layered architecture is obtained (Fig. 2) which has close contacts between the non-coordinating nitro O atoms [ $\text{O}5 \cdots \text{O}6^{\text{i}} = 2.986 (5) \text{ \AA}$ ; symmetry code: (i)  $x, \frac{1}{2} - y, -\frac{1}{2} + z$ ]. This kind of  $\text{O} \cdots \text{O}$  contact has been reported in 1,2,3,4,5,7-hexanitrocubane (Gilardi *et al.*, 2002).

In addition, there is an intramolecular O—H $\cdots$ O hydrogen bond between the bound water molecule and one nitro O atom (O5) and an intermolecular C—H $\cdots$ O hydrogen bond utilizing the other nitro O atom (O6) (Table 2). The latter provides a weak link between the two-dimensional layers and has a graph-set motif of  $R_2^2(10)$  (Bernstein *et al.*, 1995). A similar layered coordination polymer has been reported in polymeric diaquatetrakis( $\mu$ -benzene-1,2-dicarboxylato)di- $\mu$ -nitrate-pentastrontium(II) (Stein & Ruschewitz, 2005), where the two-dimensional layers are only held together by weak van der Waals forces.



**Figure 2**

The two-dimensional layered framework in (I), viewed down the  $b$  axis. H atoms have been omitted for clarity.

## Experimental

An aqueous solution (5 ml) of  $\text{SrCl}_2\cdot 6\text{H}_2\text{O}$  (0.2666 g, 1 mmol) was added dropwise to a hot aqueous solution (3 ml) of  $\text{NO}_2\text{-H}_2\text{BDC}$  (0.2210 g, 1 mmol). After mixing for 5 min, an aqueous solution (2 ml) of  $\text{NaN}_3$  (0.0650 g, 1 mmol) was slowly added. The resulting mixture was stirred for 10 min at room temperature and then filtered. Colourless block-shaped crystals of (I) were obtained from the filtrate at room temperature after four weeks. See the archived CIF for a warning and IR data.

### Crystal data

$[\text{Sr}(\text{C}_8\text{H}_3\text{NO}_6)(\text{H}_2\text{O})]$	$V = 1991.2 (6) \text{ \AA}^3$
$M_r = 314.75$	$Z = 8$
Orthorhombic, $Pccn$	Mo $K\alpha$ radiation
$a = 11.0883 (19) \text{ \AA}$	$\mu = 5.44 \text{ mm}^{-1}$
$b = 26.405 (5) \text{ \AA}$	$T = 294 (2) \text{ K}$
$c = 6.8010 (12) \text{ \AA}$	$0.28 \times 0.18 \times 0.16 \text{ mm}$

### Data collection

Bruker SMART CCD area-detector diffractometer	9126 measured reflections
Absorption correction: multi-scan ( <i>SADABS</i> ; Sheldrick, 1996)	1747 independent reflections
$T_{\text{min}} = 0.311, T_{\text{max}} = 0.416$	1387 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.076$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$	3 restraints
$wR(F^2) = 0.081$	H-atom parameters constrained
$S = 1.15$	$\Delta\rho_{\text{max}} = 0.74 \text{ e \AA}^{-3}$
1747 reflections	$\Delta\rho_{\text{min}} = -0.77 \text{ e \AA}^{-3}$
154 parameters	

**Table 1**

Selected geometric parameters ( $\text{ \AA}, ^\circ$ ).

Sr1—O1 <sup>i</sup>	2.458 (3)	Sr1—O2 <sup>v</sup>	2.641 (3)
Sr1—O3 <sup>ii</sup>	2.510 (3)	Sr1—O4	2.783 (3)
Sr1—O4 <sup>iii</sup>	2.543 (3)	O1—C1	1.239 (5)
Sr1—O2 <sup>iv</sup>	2.604 (3)	O2—C1	1.263 (5)
Sr1—O3	2.621 (3)	O3—C8	1.249 (5)
Sr1—O7	2.636 (4)	O4—C8	1.249 (5)
O4 <sup>iii</sup> —Sr1—O2 <sup>iv</sup>	69.34 (9)	O2 <sup>iv</sup> —Sr1—O3	68.98 (9)
O4 <sup>iii</sup> —Sr1—O3	72.70 (9)		

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

**Table 2**

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

$D\text{—H}\cdots A$	$D\text{—H}$	$H\cdots A$	$D\cdots A$	$D\text{—H}\cdots A$
O7—H7A $\cdots$ O5 <sup>ii</sup>	0.87	2.47	3.294 (6)	157
C4—H4 $\cdots$ O6 <sup>vi</sup>	0.93	2.48	3.335 (6)	153

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

H atoms attached to C atoms were placed in calculated positions, with  $\text{C—H} = 0.93 \text{ \AA}$ , and allowed to ride on their parent atoms, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . H atoms attached to O atoms were located in a difference map and refined as riding in their as-found positions, with  $\text{O—H} = 0.85\text{--}0.87 \text{ \AA}$  and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$ .

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine

structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3050). Services for accessing these data are described at the back of the journal.

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