Poly[strontium(II)-μ_2-aqua-μ_5-4-carboxylatophenoxyacetato]

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In the title three-dimensional coordination polymer, [Sr(4-CPOA)(H$_2$O)]$_n$ (where 4-CPOA^{2-} is the 4-carboxylatophenoxyacetate dianion, C$_9$H$_6$O$_5$), each Sr^{II} atom displays a bicapped triangular prismatic configuration, defined by five carboxyl and one ether O atom from five different 4-CPOA^{2-} ligands, as well as two water molecules. The Sr^{II} atoms are covalently linked by 4-CPOA^{2-} ligands and water molecules, giving rise to a three-dimensional open framework. In previously studied polymers of this type, the 4-CPOA^{2-} ligand shows a variety of binding modes to metal ions, from mono- to pentadentate. In the present Sr^{II} complex, a novel hexadentate bridging mode is observed.

Comment

In recent years, great interest has been focused on the design and synthesis of coordination polymers for their intriguing architectures and favorable properties (Moulton & Zaworotko, 2001). The selected ligand is an important factor that greatly influences the structure of the coordination polymer and the functionality of the complex formed. 4-Carboxyphenoxyacetic acid (4-CPOAH$_2$) is a multidentate carboxylate
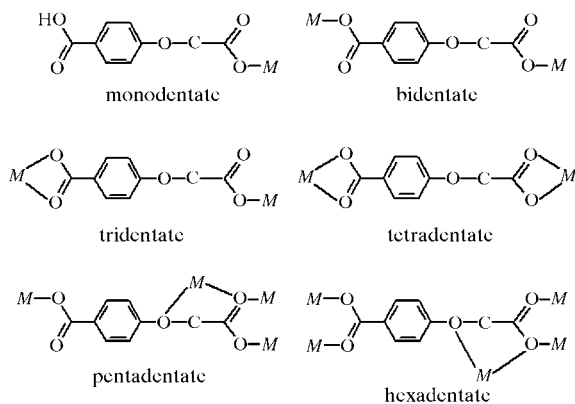
with both rigid and flexible parts, which can be used as a terminal or a bridging ligand with different coordination modes when coordinated to various metal ions (see scheme above).

Hence, 4-CPOAH$_2$ can be considered as an excellent candidate for the construction of supramolecular architectures. In previous work, we synthesized and reported some transition metal complexes containing the 4-CPOAH$_2$ ligand, such as the cobalt (Gao *et al.*, 2004*a*; Gao, Huo, Gu, Liu & Zhao, 2005), zinc (Gao *et al.*, 2004*b*; Gao, Huo *et al.*, 2004), cadmium (Gao, Huo, Gu & Zhao, 2005; Gao, Liu *et al.*, 2005), copper (Gao, Huo, Liu, Gu *et al.*, 2005), manganese (Gu, Gao, Huo *et al.*, 2004; Gao, Huo, Liu & Zhao, 2005) and nickel complexes (Gu, Gao, Zhao *et al.*, 2004), in which the 4-CPOA^{2-} ligand shows a variety of binding modes from mono- to tetradentate. On the other hand, the structures of alkali

(I)
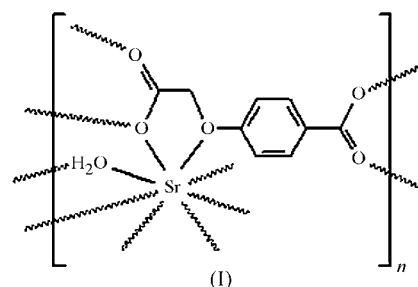
earth metal complexes have been explored less than those of the extensively investigated transition metal complexes. Recently, we reported the crystal structures of [Mg(4-CPOAH)$_2$(H$_2$O)$_4$] (Gao, Li *et al.*, 2004) and [Sr$_2$(4-CPOA)$_2$(H$_2$O)$_5$] (Gao, Huo, Zhao *et al.*, 2005), in which the 4-CPOAH$_2$ ligand is present in mono- or pentadentate binding mode. In order to explore further the coordination behavior of alkali earth metal with the 4-CPOAH$_2$ ligand, we present here an investigation of the hydrothermal synthesis and structural characterization of a novel three-dimensional Sr^{II} coordination polymer, [Sr(4-CPOA)(H$_2$O)]$_n$, (I).

As illustrated in Fig. 1, the asymmetric unit of (I) consists of one Sr^{II} ion, one 4-CPOA^{2-} dianion and one coordinated
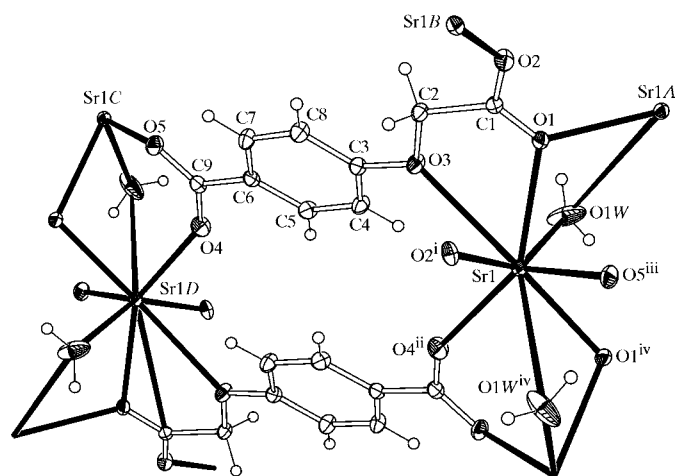

Figure 1
An *ORTEPII* (Johnson, 1976) plot of the title complex, with displacement ellipsoids drawn at the 30% probability level. [Symmetry codes: (i) $-x + \frac{3}{2}$, $y - \frac{1}{2}$, z; (ii) $-x + 1$, $-y$, $-z + 1$; (iii) x, $-y + \frac{1}{2}$, $z - \frac{1}{2}$; (iv) $-x + 1$, $y - \frac{1}{2}$, $-z + \frac{1}{2}$; (*A*) $-x + 1$, $y + \frac{1}{2}$, $-z + \frac{1}{2}$; (*B*) $-x + \frac{3}{2}$, $y + \frac{1}{2}$, z; (*C*) x, $-y + \frac{1}{2}$, $z + \frac{1}{2}$; (*D*) $-x + 1$, $-y$, $-z + 1$.]

water molecule. Each Sr^{II} atom is eight-coordinated by five carboxyl O atoms and one ether O atom from five different 4-CPOA^{2-} ligands, as well as by two bridging water molecules. The coordination environment of the Sr^{II} atom can be described as a bicapped triangular prism (Fig. 2). Table 1 presents selected coordination distances. The dihedral angle between the two basal planes (O1W/O4^{ii}/O1^{iv} and O1/O2^{i}/O5^{iii}) is 11.5 (6)° [symmetry codes: (i) $-x + \frac{3}{2}$, $y - \frac{1}{2}$, z; (ii) $-x + 1$, $-y$, $-z + 1$; (iii) x, $-y + \frac{1}{2}$, $z - \frac{1}{2}$; (iv) $-x + 1$, $y - \frac{1}{2}$, $-z + \frac{1}{2}$], and the vertical distances between the two capping atoms, O1W^{iv} and O3, and their side planes O1^{iv}/O2^{i}/O4^{ii}/O5^{iii} and O1W/O1/O2^{i}/O4^{ii} are 2.1745 (3) and 2.1910 (3) Å, respectively. The Sr—O$_{carboxyl}$ bond distances fall in the range 2.4824 (19)–2.9325 (18) Å, the longest of which (Sr1—O3) is essentially the same as the corresponding distance [2.932 (2) Å] in [Sr$_2$(4-CPOA)$_2$(H$_2$O)$_5$] (Gao, Huo, Zhao et al., 2005). The mean Sr—O1W distance [2.883 (3) Å] is somewhat longer than that in [Sr(Hbtc)(H$_2$O)$_2$]·0.5H$_2$O [mean 2.714 (9) Å; Hbtc is benzene-1,3,5-tricarboxylate; Plater et al., 1998], in which the Sr^{II} atom is nine-coordinated by two bidentate carboxylate groups, three monodentate carboxylate groups and two water molecules.

In (I), the terminal 4-CPOA^{2-} groups adopt two different coordination modes, namely bridging bidentate and bridging tetradentate. In the first case, the O4/C9/O5 carboxylate group, in a bis-monodentate mode, is coordinated to atoms Sr1C and Sr1D through carboxyl atoms O5 and O4, the Sr1C···Sr1D [symmetry codes: (C) x, $-y + \frac{1}{2}$, $z + \frac{1}{2}$; (D) $-x + 1$, $-y$, $-z + 1$] separation being 4.131 (3) Å. In the second case, the phenoxyacetate group (O1/C1/O2) chelates atom Sr1
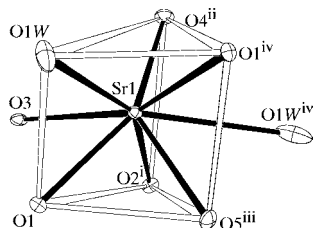
through ether atom O3 and carboxyl atom O1, bridges to a neighboring atom Sr1A through carboxyl atom O1, and links to atom Sr1B through carboxyl atom O2, the Sr1···Sr1A and Sr1A···Sr1B separations [symmetry codes: (A) $-x + 1$, $y + \frac{1}{2}$, $-z + \frac{1}{2}$; (B) $-x + \frac{3}{2}$, $y + \frac{1}{2}$, z] being 4.131 (3) and 6.200 (3) Å, respectively. Thus, the 4-CPOA^{2-} ligand provides a total of six binding sites to link five Sr^{II} atoms, giving rise to a five-membered chelate ring, O1/C1/C2/O3/Sr1, while the ligand has a pentadentate coordination mode in [Sr$_2$(4-CPOA)$_2$(H$_2$O)$_5$] (Gao, Huo, Zhao et al., 2005). The dihedral angles between the two carboxyl groups and the aromatic ring are 9.8 (6) (O1/C1/O2) and 14.6 (6)° (O4/C9/O5). The torsion angle of the oxyacetate group (C3—O3—C2—C1) is −168.8 (2)°, showing that the 4-CPOA^{2-} ligand is planar.

Carboxyl atom O1^{iv} and water molecule O1W^{iv} link adjacent Sr^{II} atoms to afford one Sr$_2$O$_2$ four-membered ring and two Sr$_2$O$_3$C six-membered rings [Sr···Sr = 4.131 (3) Å], and are further linked by a pair of 4-CPOA^{2-} ligands to produce a centrosymmetric macrocyclic structure, with an Sr1···Sr1D distance of 10.049 (3) Å and a shortest centroid–centroid separation between two inversion-related benzene rings of 4.949 (3) Å. As a consequence of the 4-CPOA^{2-} bridges, polymer (I) has an extended three-dimensional open framework, with alternating 'organic' and 'inorganic' sheets (Fig. 3).

Besides the rigid bonding network defining the three-dimensional structure, there are a number of softer non-bonding interactions present. Both H atoms of the coordinated water molecule are involved in hydrogen bonding (H1W2 in a bifurcated mode), interacting with both sides of the 4-CPOA^{2-} ligand through carboxylate atoms O2 and O5 (Table 2). Moreover, there also exist π–π stacking interactions between adjacent aromatic rings along the b axis, with a shortest centroid–centroid separation of 3.800 (3) Å.

Figure 2
The coordination polyhedron of the Sr atom in the title complex. [Symmetry codes: (i) $-x + \frac{3}{2}$, $y - \frac{1}{2}$, z; (ii) $-x + 1$, $-y$, $-z + 1$; (iii) x, $-y + \frac{1}{2}$, $z - \frac{1}{2}$; (iv) $-x + 1$, $y - \frac{1}{2}$, $-z + \frac{1}{2}$.]
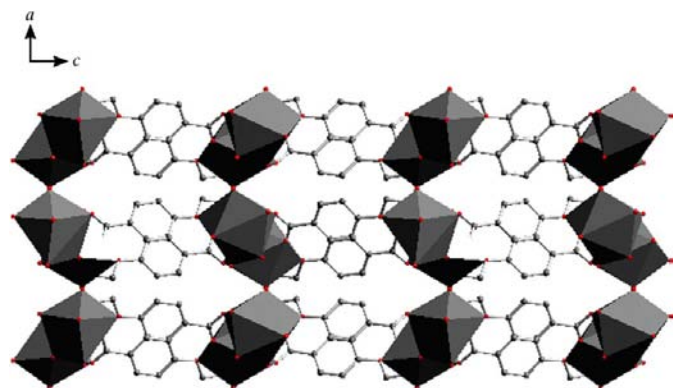

Figure 3
The packing of the title complex, viewed along the b axis. H atoms have been omitted.

Experimental

An aqueous solution (30 ml) of SrCO$_3$ (2.95 g, 20 mmol) and 4-CPOAH$_2$ (3.92 g, 20 mmol) was prepared, stirred for 1 h, sealed in a 50 ml Teflon-lined stainless steel bomb and finally held at 423 K for 3 d. The bomb was cooled naturally to room temperature and colorless prismatic crystals of (I) were obtained. Analysis calculated for C$_9$H$_8$O$_6$Sr: C 36.06, H 2.69%; found: C 36.10, H 2.72%.

Crystal data

[Sr(C$_9$H$_6$O$_5$)(H$_2$O)]	Mo $K\alpha$ radiation
$M_r = 299.77$	Cell parameters from 16445
Orthorhombic, $Pbca$	reflections
$a = 12.028$ (2) Å	$\theta = 3.4$–27.5°
$b = 7.4280$ (15) Å	$\mu = 5.48$ mm^{-1}
$c = 22.062$ (4) Å	$T = 295$ (2) K
$V = 1971.1$ (6) Å^3	Prism, colorless
$Z = 8$	$0.35 \times 0.26 \times 0.19$ mm
$D_x = 2.020$ Mg m^{-3}	

Data collection

Rigaku R-AXIS RAPID	2263 independent reflections
diffractometer	1874 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.059$
Absorption correction: multi-scan	$\theta_{max} = 27.5°$
(*ABSCOR*; Higashi, 1995)	$h = -15 \rightarrow 15$
$T_{min} = 0.201$, $T_{max} = 0.363$	$k = -9 \rightarrow 9$
17416 measured reflections	$l = -28 \rightarrow 28$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0309P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.029$	$+ 1.3751P]$
$wR(F^2) = 0.063$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.001$
2263 reflections	$\Delta\rho_{max} = 0.49$ e Å^{-3}
151 parameters	$\Delta\rho_{min} = -0.34$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected interatomic distances (Å).

Sr1—O1^{iv}	2.5555 (17)	Sr1—O1W	2.517 (2)
Sr1—O1	2.5561 (17)	Sr1—O1W^{iv}	3.249 (3)
Sr1—O2^{i}	2.4824 (19)	O1—C1	1.250 (3)
Sr1—O3	2.9325 (18)	O2—C1	1.246 (3)
Sr1—O4^{ii}	2.4926 (19)	O4—C9	1.263 (3)
Sr1—O5^{iii}	2.5411 (19)	O5—C9	1.253 (3)

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1W—H1W1$\cdots$O5^{v}	0.85 (3)	2.01 (3)	2.743 (3)	145 (4)
O1W—H1W2$\cdots$O2^{iv}	0.84 (3)	2.22 (3)	2.907 (3)	139 (4)
O1W—H1W2$\cdots$O5^{vi}	0.84 (3)	2.43 (3)	3.121 (3)	140 (4)

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

C-bound H atoms were placed in calculated positions, with C—H = 0.93 or 0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$, and were refined in the riding-model approximation. Water H atoms were located in a difference map and refined with O—H and H$\cdots$H distance restraints of 0.85 (1) and 1.39 (1) Å, respectively, and with $U_{iso}(H) = 1.5U_{eq}(O)$.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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