

catena-Poly[[aquabarium(II)]- μ -aqua-bis(μ -2'-carboxybiphenyl-2-carboxylato)]Samia Djehni,^a Fadila Balegrone,^{a*} Achoura Guehria-Laidoudi,^a Slimane Dahaoui^b and Claude Lecomte^b

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In the title compound, $[\text{Ba}\{\text{HOOC}(\text{C}_6\text{H}_4)_2\text{CO}_2\}_2(\text{H}_2\text{O})_2]$ or $[\text{Ba}(\text{C}_{14}\text{H}_9\text{O}_4)_2(\text{H}_2\text{O})_2]$, the Ba atoms are coordinated by nine O atoms, six from two 2'-carboxybiphenyl-2-carboxylate (Hbpd^-) ligands and three from three coordinated water molecules, resulting in the formation of face-sharing distorted monocapped square antiprisms. The Hbpd^- ligands bridge the Ba atoms to form a one-dimensional helical polymer, with a $\text{Ba}\cdots\text{Ba}$ distance across the chain of 4.1386 (17) Å. Adjacent chains are parallel to each other. The two independent ligands are tetradentate and have the same coordination mode, exhibiting μ -oxo bridges and η^8 -chelation. The crystal structure is further stabilized by hydrogen bonds within each chain.

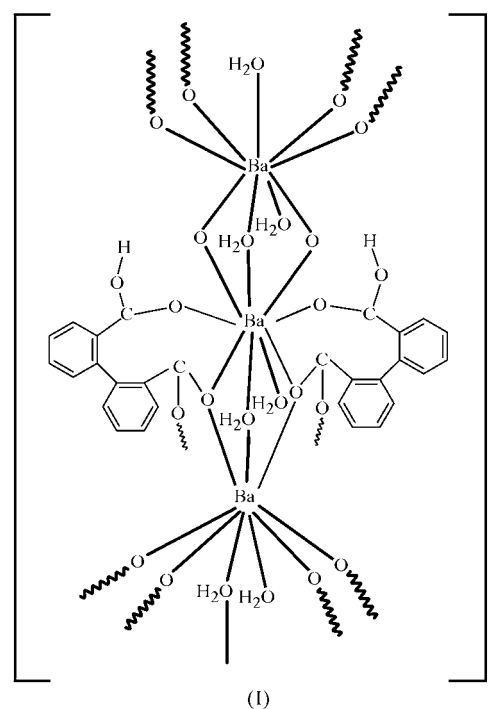
Comment

The design of supramolecular architectures employing dicarboxylic acids as ambidentate and templating ligands with metals offering interesting connectivity remains a topical research subject (Rao *et al.*, 2004). The increasing interest is principally due to the tunability of the resulting extended frameworks. Among the previously studied compounds are several layered compounds (Wan *et al.*, 2002; Benmerad, Guehria-Laïdoudi, Bernardinelli & Balegrone, 2000), single-strand polymers (Tu *et al.*, 2005; Benmerad, Guehria-Laidoudi, Balegrone *et al.*, 2000; Benmerad *et al.*, 2004*b*) and three-dimensional crosslinked polynuclear units (Pan *et al.*, 2001; Benmerad *et al.*, 2004*a*; Djehri *et al.*, 2006). These compounds typically exhibit infinite $M\text{—O—}M$ chains and several poly-membered rings, which favour interactions between the metal atoms and create various kinds of voids.

Therefore, these materials are not only microporous, bringing out interesting chemical properties (ionic exchange), but have useful magnetic (Rueff *et al.*, 2003; Mukherjee *et al.*, 2004), electronic and optical (Kim *et al.*, 2004; Thirumurugan

et al., 2004; Millange *et al.*, 2004) properties (electronic and/or magnetic exchange). These properties can be finely tuned, because the dimensionality of the framework, the interpenetration of pores and the orientation of the binding sites may be controlled, depending on synthesis conditions, as well as the characteristics of connectors and linkers.

Using this approach, we investigated the building-block methodology by using biphenyl-2,2'-dicarboxylate as a relatively flexible ligand and an alkaline-earth metal as a versatile connector. For the latter, a variable coordination number, in the range 7–12, provides the ability of adapting to many different environments. In the course of our studies on coordination polymers with interesting dimensionalities and functionalities, we have selected the barium– H_2bdpc (H_2bdpc is biphenyl-2,2'-dicarboxylic acid) system, to extend this research with the title complex, $[\text{Ba}(\text{Hbpd}^-)_2(\text{H}_2\text{O})_2]$, (I).



Complex (I) is a one-dimensional helical polymer. The asymmetric unit contains one Ba^{II} atom, two coordinating water molecules and two tritopic ligands (Hbpd^-). As shown in Fig. 1, the Ba atom is nine-coordinate. Although they are crystallographically independent, the two ligands exhibit the same coordination mode, involving only one O atom from each end functional group, forming a μ -oxo bridge through atoms O4 and O7, respectively, for ligand L1 and ligand L2, and η^8 chelation, analogous to the so-called 'malonate mode' in the α,ω -aliphatic dicarboxylates.

In the present compound, and in the absence of any bridging *exo* ligand, this connectivity seems to exist only with alkaline-earth and rare-earth biphenyldicarboxylates (Thirumurugan *et al.*, 2003, 2004; Wang *et al.*, 2004). As a consequence, a dramatic twist is observed, as shown by the helix formed by the spacer with torsion angles of -84.0 (2°) ($\text{C}2\text{—C}7\text{—C}8\text{—C}13$) in L1 and 84.8 (3°) ($\text{C}16\text{—C}21\text{—C}22\text{—C}27$) in L2.

A comparison with the biphenate compounds presenting the same connectivity shows the great distortions induced in the resulting nine-membered ring. The torsion angles between the two benzene rings are far from what has been reported (Thirumurugan *et al.*, 2003, 2004), being -5.3 (3) (C1–C2–C7–C8) and 10.3 (3)° (C14–C13–C8–C7) for L1, and 4.6 (3) (C15–C16–C21–C22) and -10.9 (3)° (C28–C27–C22–C21) for L2. Several other twists are observed within each biphenyl unit. The functional ends are inclined at angles of 52.3 (9) and 55.5 (1)° to each other owing to the helical arrangement of the spacer; between the carboxylate or the carboxyl groups and the corresponding linking benzene rings, the dihedral angles are small [40.1 (1)/ 39.3 (1) and 59.0 (6)/ 53.26 (9)°] and the two benzene rings are nearly perpendicular to one another, with dihedral angles of 82.32 (7) and 81.86 (8)°. However, this geometry is similar to that found in the pure acid (Fronczek *et al.*, 1987) and is not unusual.

The formation of helical chains in one-dimensional coordination polymers is relatively common, particularly when the connectors are running in a zigzag fashion, as in this case. The metal atom lies in the centre of two square planes formed by atoms O4, O7ⁱ, O4ⁱ and O7 (see Table 1 for symmetry code), which are the O atoms of the carboxylate functional ends, and atoms O1, O1W, O5 and OW2, comprising the O atoms of the second carboxylate groups.

The two square MO_4 and $MO_2(H_2O)_2$ structural features are almost planar [the maximum deviations being 0.0551 (8) and 0.0031 (3) Å, respectively] and nearly parallel to one another; the dihedral angle between them is 3.11 (7)°. The coordination environment of the Ba atom is completed by the O1Wⁱⁱ water molecule at the apex position of these two squares. The resulting coordination polyhedron is a distorted monocapped square antiprism. The Ba–O bond lengths present a small dispersion [2.6922 (19)– 2.9144 (15) Å] and remain within the range reported for barium carboxylate complexes (Bae *et al.*, 2002). The 36 different bond angles around the metal atom lie in the range 66.35 (4)– 142.99 (4)°, which is comparable to that for α,ω -aliphatic dicarboxylates, in

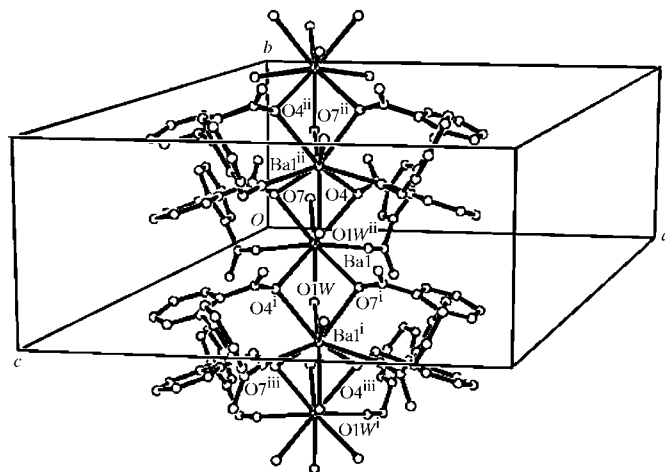


Figure 2
The one-dimensional chain of BaO₉ polyhedra, viewed along the *b* axis. [Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $x, y - 1, z$.]

the same connectivity. Fig. 2 shows the infinite one-dimensional chain and face-sharing barium polyhedra. Within the chain, each Ba atom is linked to two others *via* three bridging O atoms, one from a water molecule (O1W) and two triply coordinated atoms (O4 and O7) from carboxylate groups.

From this point of view, this network, built up from decorated chains of BaO₉ monocapped square antiprisms, is somewhat similar to the recently reported tancoite-related structures (Thirumurugan *et al.*, 2003, 2004). The Ba···Ba distance across the chain is 4.1386 (19) Å. The benzene rings belonging to the same chain are parallel to each other and the distances between these parallel rings are in the range 3.90 – 4.42 Å. Adjacent chains are parallel to each other.

There are no direct π – π interactions between the biphenyl groups within the chain, nor along adjacent chains. Several intrachain hydrogen bonds are observed. They involve, as hydrogen-bonding acceptors, the uncoordinated carboxylate atoms O3 from L1 and O8 from L2. In each ligand, the same H atom (H2 and H6, respectively) is shared between the protonated and deprotonated ends of the symmetrical ligands (Table 2). Two other, weaker, hydrogen bonds involve the O1W water molecule and the atoms that are not bonded to the metal.

Experimental

A mixture of diphenic acid (0.484 g, 2 mmol) and barium hydroxide octahydrate (0.473 g, 1.5 mmol) in water (20 ml) was heated (353–363 K) and stirred for 30 min, and the resulting mixture was filtered. Colourless single crystals were obtained after several weeks at 313 K.

Crystal data

[Ba(C₁₄H₉O₄)₂(H₂O)₂]
M_r = 655.80
 Monoclinic, *P*₂₁/*n*
a = 16.418 (5) Å
b = 7.171 (4) Å
c = 22.428 (5) Å
 β = 102.543 (5)°
V = 2577.5 (17) Å³

Z = 4
D_x = 1.690 Mg m⁻³
 Mo *K*α radiation
 μ = 1.60 mm⁻¹
T = 294 (2) K
 Prism, colourless
 0.40 × 0.10 × 0.05 mm

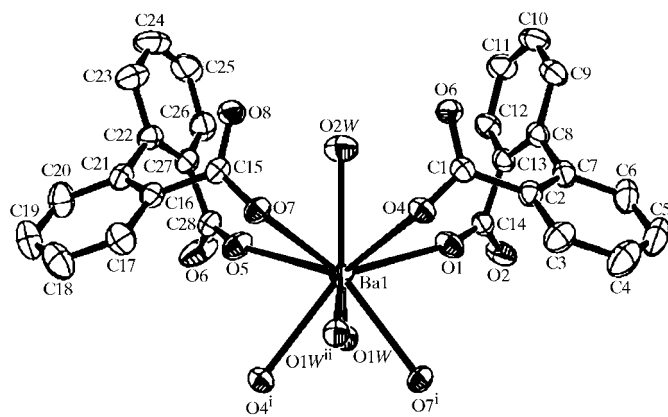


Figure 1
A view of the coordination environment around the Ba atom, showing the atom-labelling scheme and 50% probability displacement ellipsoids. [Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.]

Data collection

Nonius KappaCCD area-detector diffractometer
 ω and φ scans
 Absorption correction: empirical (using intensity measurements) (*DENZO-SMN*; Otwinowski & Minor, 1997)
 $T_{\min} = 0.619$, $T_{\max} = 0.917$

11569 measured reflections
 11547 independent reflections
 9372 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.045$
 $\theta_{\text{max}} = 35.6^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.069$
 $S = 1.04$
 11547 reflections
 370 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0177P)^2 + 2.6715P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.007$
 $\Delta\rho_{\text{max}} = 0.80 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.90 \text{ e } \text{\AA}^{-3}$

Table 1

Selected bond lengths (Å).

Ba1—O1W	2.6922 (19)	Ba1—O5	2.8113 (17)
Ba1—O7	2.7360 (16)	Ba1—O4 ⁱ	2.8136 (14)
Ba1—O4	2.7598 (17)	Ba1—O2W	2.8373 (18)
Ba1—O7 ⁱ	2.7836 (14)	Ba1—O1W ⁱⁱ	2.9144 (15)
Ba1—O1	2.8091 (15)	Ba1—Ba1 ⁱⁱ	4.1386 (17)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1W—H1A \cdots O8 ⁱⁱⁱ	0.85 (2)	1.91 (2)	2.755 (3)	173 (3)
O1W—H1B \cdots O3 ⁱⁱⁱ	0.85 (2)	1.91 (3)	2.753 (3)	175 (2)
O2—H2 \cdots O3 ⁱⁱⁱ	0.84 (2)	1.84 (2)	2.670 (3)	170 (2)
O6—H6A \cdots O8 ⁱⁱⁱ	0.85 (2)	1.84 (2)	2.677 (3)	169 (2)

Symmetry code: (iii) $x, y - 1, z$.

H atoms attached to C atoms were placed in calculated positions and treated as riding, with C—H distances of 0.95 Å and $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C})$. H atoms of water molecules and hydroxyl groups were located in a difference Fourier map and refined with an O—H distance restraint of 0.85 (1) Å and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

Data collection: *COLLECT* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction:

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3066). Services for accessing these data are described at the back of the journal.

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