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Poly[[diaquabarium(II)]-μ_5-*m*-phenylenedioxydiacetato]: a three-dimensional barium(II) coordination polymer

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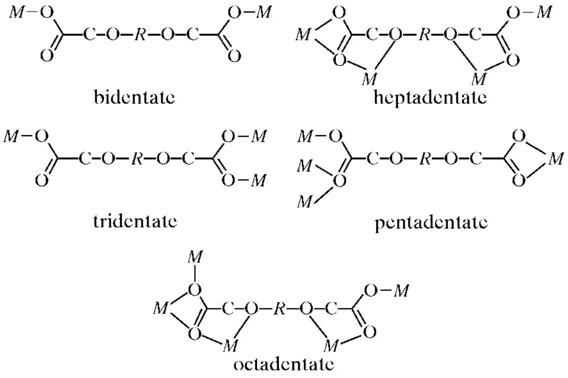
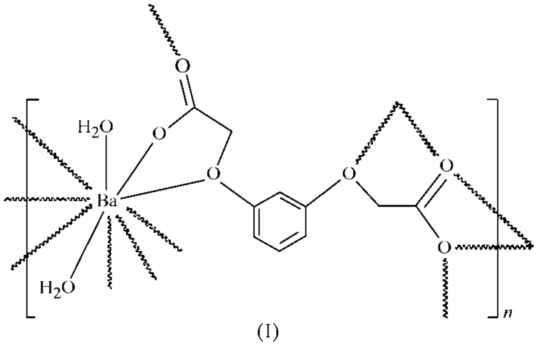
In the title coordination polymer, $[Ba(1,3\text{-BDOA})(H_2O)_2]_n$ (where 1,3-BDOA^{2-} is the *m*-phenylenedioxydiacetate dianion, $C_{10}H_8O_6$), each Ba^{II} ion is ten-coordinated by six carboxyl O atoms and two ether O atoms from different 1,3-BDOA^{2-} ligands, as well as by two water molecules, thus defining a dodecahedron. The Ba^{II} atoms are covalently linked by 1,3-BDOA^{2-} ligands in different crystallographic directions, giving rise to a three-dimensional open framework. The crystal structure is further stabilized by hydrogen bonds and π–π stacking interactions. In previously studied polymers of this type, the 1,3-BDOA^{2-} ligand showed multiple bridging modes with metal ions, including bi-, tri-, tetra- and hexadentate. The title Ba^{II} complex represents a novel three-dimensional coordination polymer constructed by octadentate bridging 1,3-BDOA^{2-} ligands.

Comment

The field of metal-ion-directed assembly of organic molecular building blocks is now providing access to new open-framework solid-state materials (Andrea, 2003). Compared with the extensively investigated transition metal coordination polymers, it is surprising to see the relatively small number of alkali earth coordination polymers in the literature (Guo *et al.*, 2002). The oxidation states and atomic radii of alkali earth metals are comparable with those of the late divalent transition metals, which could, in principle, lead to similar networks in the solid state. However, the lack of *d*-orbital electrons in alkali earth metals could result in coordination numbers greater than six, and for the larger alkali earth metals, a higher coordination number is expected (Huo *et al.*, 2004). *m*-Phenylenedioxydiacetate (1,3-BDOAH$_2$) is a potential flexible multidentate ligand containing two oxyacetate groups, which could be used as a terminal ligand or a bridging ligand with different coordination modes when coordinated to various metal ions (see scheme below). In addition to its versatile coordination modes, 1,3-BDOAH$_2$ may take part in hydrogen-bonding interactions by functioning as either a hydrogen-bond donor or acceptor, and in π–π stacking interactions *via* its benzene ring. Recently, we have reported the structures of three one-dimensional chain polymers, namely $[Cu(1,3\text{-BDOA})(bipy)(H_2O)]_n$ (Liu *et al.*, 2004), $\{[Zn(1,3\text{-BDOA})(H_2O)_2](H_2O)_2\}_n$ (Gao, Li *et al.*, 2004) and $\{[Cu(1,3\text{-BDOA})(phen)(H_2O)]\cdot 2H_2O\}_n$ (Gao, Liu *et al.*, 2004*a*), as well as three two-dimensional layer polymers, namely $[Cd(1,3\text{-BDOA})]_n$ (Gao, Liu *et al.*, 2004*b*), $[Cd(1,3\text{-BDOA})(imidazole)_2]_n$ (Gao, Liu *et al.*, 2004*c*) and $[Mn(1,3\text{-BDOA})(H_2O)_3]_n$ (Gao, Liu *et al.*, 2004*d*), within which the metal ions have tetrahedral, square-pyramidal and octahedral configurations. The work described here is an investigation into the hydrothermal synthesis and structural characterization of the title novel three-dimensional Ba^{II} coordination polymer $[Ba(1,3\text{-BDOA})(H_2O)_2]_n$, (I), in which the Ba^{II} atom has tenfold coordination and the 1,3-BDOA^{2-} dianion adopts a novel octadentate bridging mode.





(I)

As shown in Fig. 1, the asymmetric building unit of complex (I) consists of one Ba^{II} atom, one 1,3-BDOA^{2-} dianion and two coordinated water molecules. Each Ba^{II} atom is ten-coordinated by two ether O atoms, six carboxyl O atoms from different 1,3-BDOA^{2-} ligands and two water molecules. The coordination geometry can best be described as a dodecahedron (Fig. 2). The O—Ba—O angles are distributed over a broad range, *viz.* 43.13 (6)–148.23 (7)°. The Ba—O$_{carboxyl}$ distances are in the range 2.736 (2)–3.218 (2) Å (Table 1), within which the Ba—O3 and Ba—O6^{iii} distances [symmetry

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code: (iii) $x - 1, \frac{3}{2} - y, z - \frac{1}{2}$] are considerably longer than the maximum Ba—O value of 3.161 (2) Å in the complex $[Ba(H_2O)_5][Cu(C_2O_4)_2(H_2O)]$ (Bouayad *et al.*, 1995). The $Ba—O_{water}$ distances are similar to those of the complex $[Ba(Hbtc)(H_2O)_2]\cdot0.5H_2O$ [2.860 (6) and 2.877 (6) Å; Hbtc is benzene-1,3,5-tricarboxylate; Platers *et al.*, 1997], (II). In (II), the Ba^{2+} ion is coordinated by two bidentate carboxylate groups, three monodentate carboxylate groups and two water molecules.

In (I), the 1,3-$BDOA^{2-}$ group adopts two coordination modes, namely bridging tridentate and bridging pentadentate. In the first case, the phenoxyacetate group (O1/C1/O2), in a bidentate chelating mode, is coordinated to atom Ba1 through ether atom O3 and carboxyl atom O1, and joins the adjacent atom Ba1*A* through the bridging atom O2, with a Ba1···Ba1*A* separation of 6.734 (3) Å [symmetry code: (*A*) $x, \frac{3}{2} - y, z + \frac{1}{2}$]. In the second case, the phenoxyacetate group (O5/C10/O6) chelates to atom Ba1*C* through carboxyl atoms O5 and O6, bridges to a neighbouring atom Ba1*D* through atom O6, and chelates to atom Ba1*B* through ether atom O4 and carboxyl atom O5, with the Ba1*B*···Ba1*C* and Ba1*C*···Ba1*D* separations being 4.755 (3) Å [symmetry codes: (*B*) $1 - x, 1 - y, 1 - z$; (*C*) $x + 1, \frac{3}{2} - y, z + \frac{1}{2}$; (*D*) $1 - x, 2 - y, 1 - z$]. The Ba1···Ba1*C* separation is 12.895 (3) Å. Thus, the 1,3-$BDOA^{2-}$ ligand provides a total of eight binding sites to link five Ba atoms and give two five-membered chelate rings (O1/C1/C2/O3/Ba1 and O4/C9/C10/O5/Ba1*B*) and one four-membered ring (C10/O5/Ba1*C*/O6). The two five-membered chelate rings are non-planar, while the four-membered chelate ring is essentially planar, with an r.m.s. deviation of 0.07 (3) Å. The dihedral angles between the carboxyl groups and the aromatic ring are 11.30 (7) (O1/C1/O2) and 62.28 (7)° (O6/C10/O5), respectively. One oxyacetate group and the aromatic ring are almost coplanar, with a torsion angle of −177.7 (3)° (C3—O3—C2—C1), while the other oxyacetate group and the benzene ring are not perfectly coplanar, with a torsion angle of −153.1 (3)° (C7—O4—C9—C10).

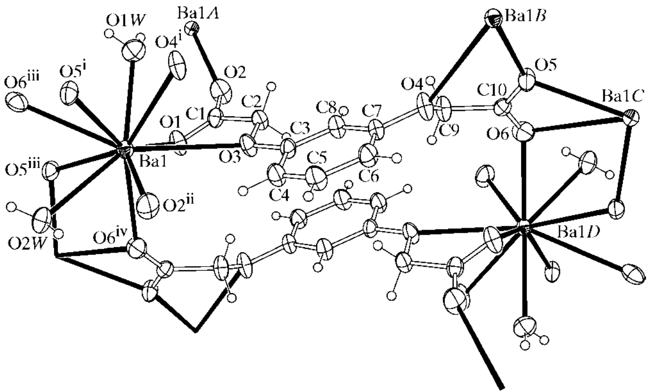

Figure 1
A view of the title complex, with displacement ellipsoids drawn at the 30% probability level. [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $x, \frac{3}{2} - y, z - \frac{1}{2}$; (iii) $x - 1, \frac{3}{2} - y, z - \frac{1}{2}$; (iv) $1 - x, 2 - y, 1 - z$; (*A*) $x, \frac{3}{2} - y, z + \frac{1}{2}$;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

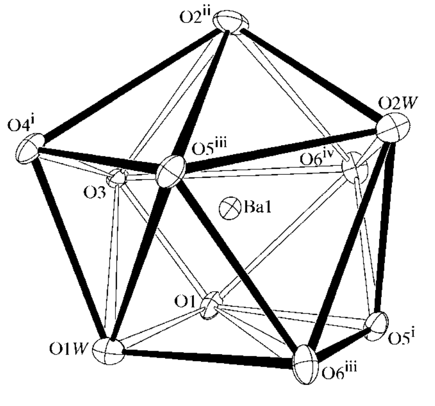

Figure 2
The coordination dodecahedron of the Ba atom in (I). [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $x, \frac{3}{2} - y, z - \frac{1}{2}$; (iii) $x - 1, \frac{3}{2} - y, z - \frac{1}{2}$; (iv) $1 - x, 2 - y, 1 - z$.]

Adjacent Ba^{II} atoms share carboxyl atoms O6^{iv} and O5^{iii} [symmetry code: (iv) $1 - x, 2 - y, 1 - z$], to afford a Ba_2O_2 four-membered ring [Ba···Ba = 4.755 (3) Å], and are further linked by a pair of 1,3-$BDOA^{2-}$ ligands to produce a centrosymmetric macrocyclic structure. As a consequence of the 1,3-$BDOA^{2-}$ bridges, polymer (I) has an extended three-dimensional open framework, with alternating 'organic' and 'inorganic' sheets (Fig. 3). There are inorganic sheets lying parallel to the (011) plane at $x = -1, 0, 1$, *etc.*, and which contain all the hydrogen bonds (Table 2). Intermolecular hydrogen-bond interactions are found between the water molecule and the carboxylate O atoms [O···O = 2.748 (3)–3.085 (4) Å and O—H···O = 127 (4)–176 (4)°]. Between these inorganic sheets there are organic sheets, which are also

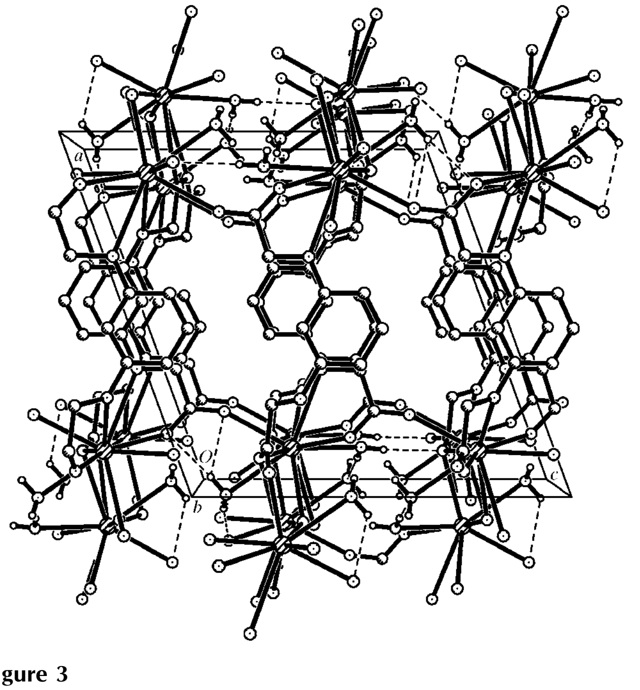

Figure 3
A packing diagram for (I). Intramolecular hydrogen bonds are shown as dashed lines. H atoms attached to C atoms have been omitted.

parallel to (011) at $x = -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$, *etc*. The shortest centroid–centroid separation between inversion-related aromatic rings is 3.495 (3) Å and the shortest plane–plane separation between aromatic rings at (x, y, z) and $(1 - x, 1 - y, 1 - z)$ is 3.341 (3) Å, indicating some π–π stacking interactions between organic sheets. These weak supramolecular interactions, together with the coordinate-covalent interactions between metal ions and organic ligands, strengthen the stability of the whole crystal structure.

Experimental

m-Phenylenedioxydiacetic acid was prepared following the method described for the synthesis of *o*-phenylenedioxydiacetic acid by Mirci (1990). $BaCl_2 \cdot 2H_2O$ (2.40 g, 10 mmol), pyridine (1 ml) and 1,3-$BDOAH_2$ (2.26 g, 10 mmol) were dissolved in water (30 ml). The mixture was sealed in a 50 ml Teflon-lined stainless steel bomb and held at 393 K for 5 d. The bomb was allowed to cool naturally to room temperature and colourless prismatic crystals of (I) were obtained. Analysis calculated for $C_{10}H_{12}BaO_8$: C 30.21, H 3.04%; found: C 30.17, H 3.08%.

Crystal data

$[Ba(C_{10}H_8O_6)(H_2O)_2]$
$M_r = 397.53$
Monoclinic, $P2_1/c$
$a = 13.476$ (3) Å
$b = 7.3396$ (15) Å
$c = 13.166$ (3) Å
$\beta = 110.00$ (3)°
$V = 1223.7$ (5) Å^3
$Z = 4$

$D_x = 2.158$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 10381 reflections
$\theta = 3.2$–27.4°
$\mu = 3.28$ mm^{-1}
$T = 295$ (2) K
Prism, colourless
0.38 × 0.25 × 0.19 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.379$, $T_{max} = 0.535$
10955 measured reflections

2787 independent reflections
2553 reflections with $I > 2\sigma(I)$
$R_{int} = 0.045$
$\theta_{max} = 27.5°$
$h = -17 \rightarrow 17$
$k = -9 \rightarrow 9$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.073$
$S = 1.05$
2787 reflections
184 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0476P)^2 + 0.631P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.17$ e Å^{-3}
$\Delta\rho_{min} = -0.99$ e Å^{-3}

Table 1
Selected geometric parameters (Å).

Ba1—O1	2.778 (2)	Ba1—O5^{ii}	2.736 (2)
Ba1—O2^{i}	2.781 (3)	Ba1—O6^{iv}	2.795 (2)
Ba1—O3	3.218 (2)	Ba1—O6^{iii}	3.173 (3)
Ba1—O4^{ii}	3.146 (2)	Ba1—O1*W*	2.794 (2)
Ba1—O5^{iii}	2.789 (2)	Ba1—O2*W*	2.876 (3)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O1*W*—H1*W*1···O6^{v}	0.85 (3)	2.18 (2)	2.986 (4)	158 (4)
O1*W*—H1*W*2···O2*W*^{vi}	0.85 (3)	1.93 (3)	2.775 (4)	176 (4)
O2*W*—H2*W*1···O1^{vi}	0.85 (3)	1.91 (3)	2.748 (3)	168 (4)
O2*W*—H2*W*2···O1^{i}	0.84 (3)	2.25 (4)	3.085 (4)	173 (3)
O2*W*—H2*W*2···O2^{i}	0.84 (3)	2.41 (4)	2.995 (4)	127 (4)

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

Water H atoms were located in a difference map and refined with O—H and H···H distance restraints of 0.85 (1) and 1.39 (1) Å, respectively, and with $U_{iso}(H) = 1.5U_{eq}(O)$. 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. The largest residual peak (1.17 e Å^{-3}) is close to the Ba atoms.

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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1847). Services for accessing these data are described at the back of the journal.

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