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Poly[triaquatri-μ-hippurato-hippuratodibarium]

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.008 Å
R factor = 0.037
wR factor = 0.101
Data-to-parameter ratio = 12.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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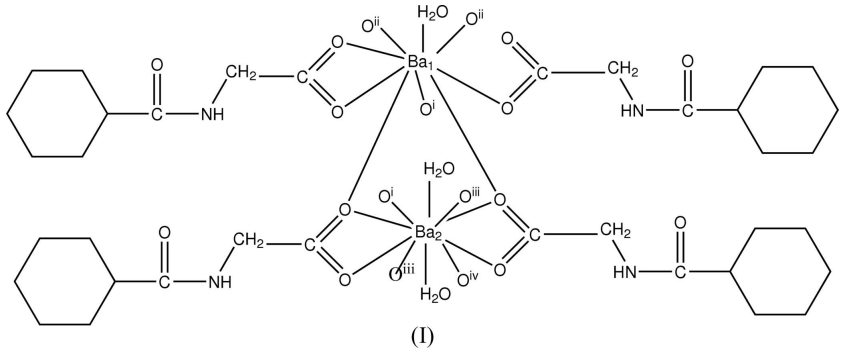
The title compound, $[Ba_2(C_9H_8NO_3)_4(H_2O)_3]$, has two Ba atoms and four hippurate ligands in the asymmetric unit of the structure, along with three water molecules. The coordination polyhedra around the two Ba atoms can be described as one involving nine O atoms in a distorted monocapped square antiprism and the other involving ten O atoms in a pentagonal pyramid placed over a distorted rectangle. There are numerous N—H···O and O—H···O bonds in the crystal structure.

Comment

Hippuric acid (the amino acid serine attached to a benzene ring) is formed in mammals during the 'detoxification' of benzoic acid by conjugation with glycine. Previous studies of hippuric acid report X-ray crystallographic and optical data and the molecular and crystal structures (Ringertz, 1971; Harrison *et al.*, 1972; Curie & Macdonald, 1974). A survey of the Cambridge Structural Database (Version 5.23; Allen, 2002) reveals that crystallographic data are known only for a few Cu, Ni and Co complexes of hippuric acid. The present work reports the crystal structure of the title barium hippurate, (I). This work is part of a systematic investigation of the structures of the metal complexes of hippuric acid.



(I)

In the structure of (I) (Fig. 1), there are two Ba atoms (Ba1 and Ba2), which are coordinated to nine and ten O atoms, respectively. For Ba1, eight O atoms come from six different hippurate anions, while for Ba2, eight O atoms come from four different hippurate anions, the remainder being from water molecules. The Ba—O distances range from 2.702 (3) to 3.072 (3) Å.

The coordination polyhedra around atoms Ba1 and Ba2 can be described as a distorted monocapped square antiprism and a pentagonal pyramid placed over a distorted rectangle, respectively. In the Ba—O coordination, one set of hippurate anions (type I) contributes both of their carboxyl O atoms

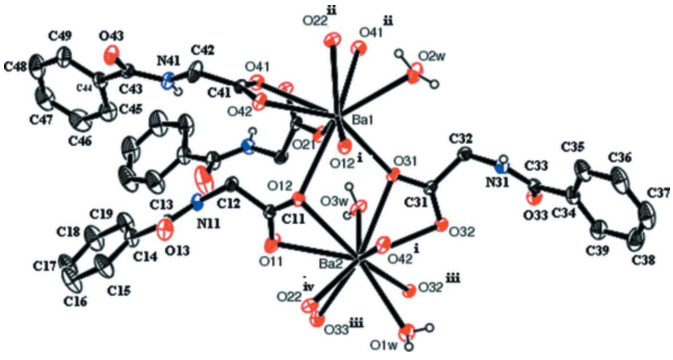


Figure 1
Part of the structure of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 15% probability level. H atoms on water molecules and amide N atoms are retained; other H atoms have been omitted for clarity. The completed coordination spheres for Ba atoms are shown. [Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $1-x, 1-y, 1-z$; (iii) $-x, -y, -z+1$; (iv) $x-1, y, z$.]

towards coordination to three different Ba atoms, whereas the other set (type II) contributes three of their O atoms, two from the carboxyl group and one from the peptide group, for coordination with two different Ba atoms.

In the packing of the polyhedra, Ba1-centred polyhedra form a linear zigzag chain running parallel to the *a* axis and sharing the edge formed by the atoms O12/O12^{i} and O41/O41^{ii} alternately. These chains are interconnected by Ba2-centred polyhedra, sharing the edge formed by the atoms O32/O32^{iii} running parallel to the *b* axis. (Symmetry codes are as given in Table 1 and Fig. 1.)

Among the four hippurate anions in (I), three belong to type I and one belongs to type II. The differences in the configurations of the four hippurate anions can be understood by the twisting of different planes. We define plane 1 as the benzene ring, plane 2 as the peptide plane and plane 3 as the carboxyl plane. For example, for hippurate anion 1, planes 1, 2 and 3 are the atoms C14–C19, O11/C13/N11/C12 and C11/O11/O12, respectively. The differences in the configurations of the hippurate anions (Table 2) may be attributed to the different types of coordination with the Ba atoms and also to the hydrogen bonding. Table 1 lists the possible N—H···O and O—H···O hydrogen bonds (between two hippurate anions and between hippurate anions and water molecules).

Experimental

Colourless single crystals of (I) were grown as transparent blocks from a saturated aqueous solution containing barium hydroxide and hippuric acid in a 1:1 stoichiometric ratio.

Crystal data

$[Ba_2(C_9H_8NO_3)_4(H_2O)_3]$
$M_r = 1041.37$
Triclinic, $P\overline{1}$
$a = 8.6447\ (7)$ Å
$b = 11.0825\ (4)$ Å
$c = 21.0332\ (9)$ Å
$\alpha = 75.974\ (8)^\circ$
$\beta = 88.987\ (9)^\circ$
$\gamma = 84.435\ (6)^\circ$
$V = 1945.76\ (19)$ Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 2.09$ mm^{-1}
$T = 293\ (2)$ K
0.19 × 0.16 × 0.11 mm

Data collection

Nonius MACH3 four-circle diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.679$, $T_{max} = 0.795$
8368 measured reflections
6866 independent reflections
6118 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.101$
$S = 1.07$
6866 reflections
538 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 2.46$ e Å^{-3}
$\Delta\rho_{min} = -2.11$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N31—H31···O13^{i}	0.86	2.14	2.894 (4)	147
O2W—H2A···O13^{i}	0.861 (10)	1.934 (16)	2.783 (4)	169 (6)
N41—H41···O2W^{ii}	0.86	2.55	3.171 (5)	130
O2W—H2B···O22^{ii}	0.861 (10)	2.11 (5)	2.799 (4)	137 (6)
O1W—H1A···O3W^{iii}	0.858 (10)	2.043 (12)	2.901 (4)	177 (6)
O1W—H1B···O21^{iv}	0.851 (10)	2.53 (4)	3.139 (4)	129 (4)
O3W—H3B···O43^{v}	0.857 (10)	2.023 (18)	2.861 (4)	166 (5)
O3W—H3A···O21	0.856 (10)	1.942 (11)	2.797 (4)	177 (4)
N11—H11···O23	0.86	1.98	2.820 (5)	166

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

Table 2
Comparison of angles (°) between different planes in (I), illustrating the differences in the configurations of hippuric acids 1–4.

Name	Planes 1 and 2	Planes 2 and 3
Hippuric acid-1	15.1 (3)	82.7 (3)
Hippuric acid-2	26.4 (2)	66.1 (3)
Hippuric acid-3	24.9 (3)	70.4 (3)
Hippuric acid-4	27.7 (2)	36.5 (3)

The water-bound H atoms were located in a difference Fourier map and the O— bonds were restrained to be 0.86 (1) Å. N- and C-bound H atoms were placed in calculated positions, with C—H = 0.93–0.97 Å and N—H = 0.86 Å, and allowed to ride on their carrier atoms, with $U_{iso} = 1.2U_{eq}$(C,N) for CH_2, CH and NH groups.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Curie, M. & Macdonald, A. L. (1974). *J. Chem. Soc. Perkin Trans. 2*, pp. 784–787.

Enraf–Nonius (1994). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Harms, K. & Wocadlo, S. (1996). *XCAD4*. University of Marburg, Germany.
Harrison, W., Rettig, S. & Trotter, J. (1972). *J. Chem. Soc. Perkin Trans. 2*, pp. 1036–1040.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Ringertz, H. (1971). *Acta Cryst.* B**27**, 285–291.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.