metal-organic compounds

catena-Poly[[[N-(4-amino-1,6-dihydro-1-methyl-5-nitroso-6-oxopyrimidin-2-yl)-(S)-glutamato]hexaaquabarium]-μ-N-(4-amino-1,6-dihydro-1-methyl-5-nitroso-6-oxopyrimidin-2-yl)-(S)-glutamato]: coordination polymer chains linked into a three-dimensional framework by N—H···O and O—H···O hydrogen bonds

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In the title complex, $[Ba(C_{10}H_{12}N_5O_6)_2(H_2O)_6]_n$, the Ba atom is nine-coordinated by six water ligands and three carboxylate O atoms. The Ba^{2+} cations and the anionic glutamate ligands form coordination polymer chains, and these chains are linked by pairs of N—H···O hydrogen bonds and pairs of O—H···O hydrogen bonds to form a continuous three-dimensional framework of cations and anions, which is reinforced by hydrogen bonds involving the water molecules.

Comment

In view of the contrast between the structural motifs found in a range of *N*-(6-amino-3,4-dihydro-3-methyl-5-nitroso-4-oxopyrimidin-2-yl) derivatives of simple amino acids on the one
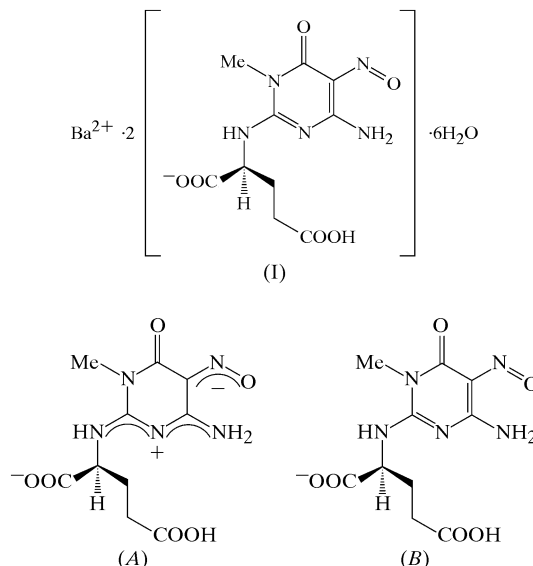
hand (Low *et al.*, 2000), and their hydrated metal(II) salts on the other (Godino Salido *et al.*, 2004), we have now investigated the title barium complex, (I), derived from *N*-(6-amino-3,4-dihydro-3-methyl-5-nitroso-4-oxopyrimidin-2-yl)-(S)-glutamic acid, (II) [(S)-glutamic acid is (S)-(+)-2-aminopentane-1,5-dioic acid]. We have recently reported the molecular and supramolecular structure of (II) (Arranz Mascarós *et al.*, 2003), where the molecules are linked into a three-dimensional framework by a combination of three hydrogen bonds, one each of the O—H···O, O—H···N and N—H···O types. A feature of interest here is that a rather short and nearly symmetrical O—H···O hydrogen bond, augmented by a rather weaker N—H···O hydrogen bond, links the molecules into double helices, which are themselves linked by the O—H···N hydrogen bond to form the framework.
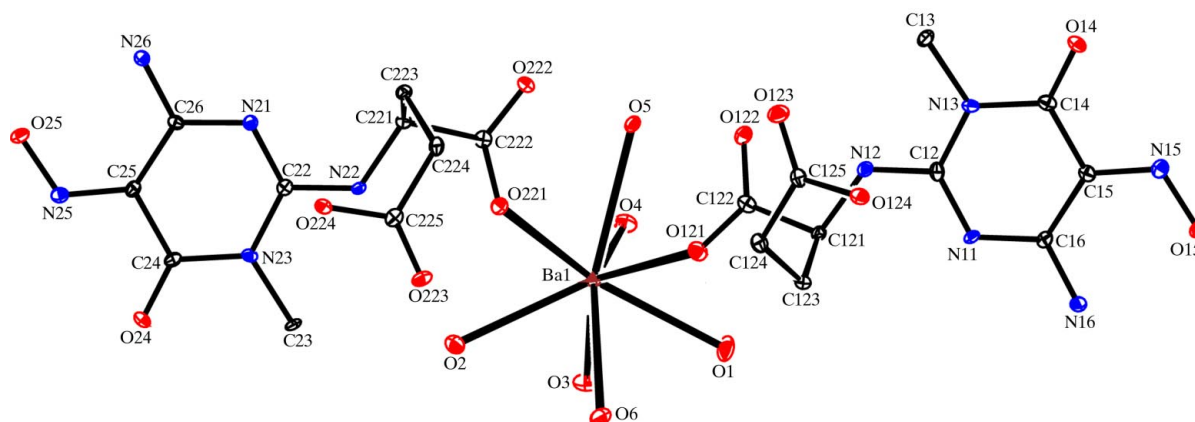

Figure 1
The independent components of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and, for the sake of clarity, H atoms have been omitted.

In compound (I) (Fig. 1), the Ba atom is nine-coordinate. The ligating atoms are all oxygen, namely three carboxyl O atoms from three different glutamate ligands together with the O atoms from six water molecules (Table 1). The anion containing atom O221 (Fig. 1) bridges pairs of Ba centres, while the anion containing atom O121 is bonded to only one Ba atom. The irregular coordination (Fig. 2) is probably best described as a distorted monocapped square antiprism, in which atom O121 is the capping atom.

It is of interest to note the subtle effect upon the metal coordination of the amino acid component of the anionic ligand. In the barium complex derived from the glycine analogue of (II), the metal is eight-coordinate, while in the complexes formed by the serine and methionine analogues, the Ba atom is ten-coordinate (Godino Salido et $al.$, 2004). Moreover, the mean Ba—O distances in these complexes for eight-, nine- and ten-coordination are 2.777, 2.836 and 2.881 Å, respectively. The trend in these values closely follows the increase with coordination number in the radius of Ba^{2+}, $viz.$ 1.42, 1.47 and 1.52 Å for eight-, nine- and ten-coordination, respectively (Shannon & Prewitt, 1969). A further difference arises within the composition of the metal coordination sphere. Nitroso O atoms are coordinated to the Ba centres in the complexes of the glycine- and methionine-based ligands, but not in those of the serine- and glutamic acid-based ligands.

Both of the organic ligands in (I) show the pattern of bond distances (Table 1) which is characteristic of amino–nitroso–pyrimidines. Thus, the bonds Nn1—Cn2 (n = 1 or 2), which are formally double bonds, are longer than the bonds Cn2—Nn2, Cn6—Nn6 and Cn6—Nn1, all of which are formally single bonds, while the bonds Cn2—Nn3 and Nn3—Cn4 are longer than all of the other C—N bonds in the system. In addition, the bonds Cn4—Cn5 and Cn5—Cn6, which are formally single and double bonds, respectively, are very similar in length. Finally, the bonds Cn5—Nn5 and Nn5—On5, which again are formally single and double bonds, respectively, differ in length by less than 0.06 Å. These observations, taken together, indi-
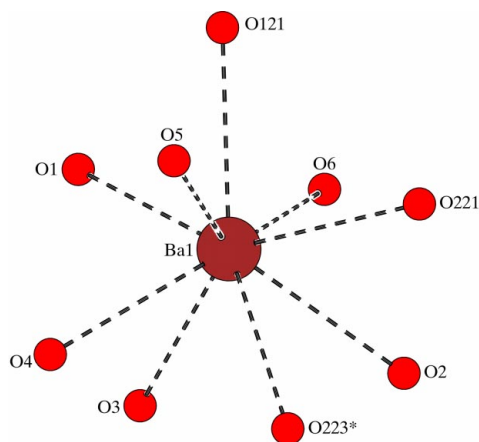
cate that the polarized form (A) (see scheme) is an important contributor to the overall molecular electronic structure, alongside the classically localized form (B). The C—O distances at C125 and C225 are fully consistent with the locations of the carboxyl H atoms as deduced from difference maps. The C—O distances at C122 and C222 are fully consistent with their carboxylate formulations.

Within each of the organic ligands, there are two intra-molecular hydrogen bonds, both of the N—H···O type (Table 2). Amino atoms N16 and N26 act as hydrogen-bond donors via atoms H16B and H26B, respectively, to nitroso atoms O15 and O25, so forming an S(6) (Bernstein et $al.$, 1995) motif in each ligand. Each ligand adopts a synclinal conformation about the Cn21—Cn23 and Cn23—Cn24 bonds, possibly associated with the coordination and hydrogen-bonding behaviour of these ligands. The overall conformation of the two ligands is very close to twofold rotational symmetry, deviating significantly only around the bonds Cn21—Cn22, where the Nn2—Cn21 and Cn22—On21 bonds are anti-periplanar when n = 1 and synperiplanar when n = 2 (Table 1 and Fig. 1).

The metal ions and the organic ligands together form a three-dimensional structure, the formation of which is readily analysed in terms of three rather simple one-dimensional sub-structures. The Ba atom at (x, y, z) is coordinated by the carboxylate atoms O121 and O221 in the organic ligands at (x, y, z) and also by the carboxyl atom O223 in the type 2 ligand at (x, 1 + y, z). In this manner, a one-dimensional coordination polymer in the form of a C(8) chain (Starbuck et $al.$, 1999) running parallel to the [010] direction is generated by translation (Fig. 3).

The cations and anions of (I) are linked into a three-dimensional framework by means of paired N—H···O and paired O—H···O hydrogen bonds. Amino atoms N16 and

Figure 2
The coordination of the Ba atom in (I). The atom marked with an asterisk (*) is at the symmetry position (x, 1 + y, z).
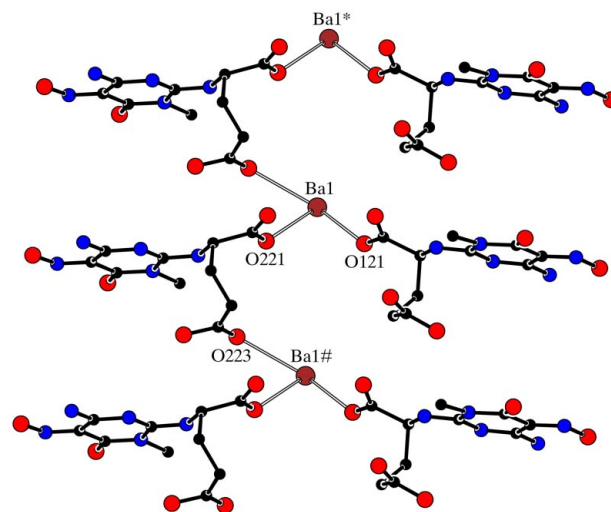
Figure 3
Part of the crystal structure of (I), showing the formation of a coordination polymer chain along [010]. For the sake of clarity, the water molecules and the H atoms have been omitted, as has the unit-cell outline. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions (x, 1 + y, z) and (x, y − 1, z), respectively.

N26 in the glutamate ligands at (x, y, z) acts as donors, *via* atoms H16A and H26A, respectively, to carbonyl atoms O14 at $(x - 1, y, z)$ and O24 at $(1 + x, y, z)$, so generating by translation a molecular ladder running parallel to the [100] direction. Within this ladder, a pair of antiparallel $C(6)$ chains (Bernstein *et al.*, 1995) acts as the uprights, while the Ba^{2+} cations lie at the centres of the rungs (Fig. 4). This motif can be alternatively described as a chain of edge-fused $R_2^2(36)$ rings.
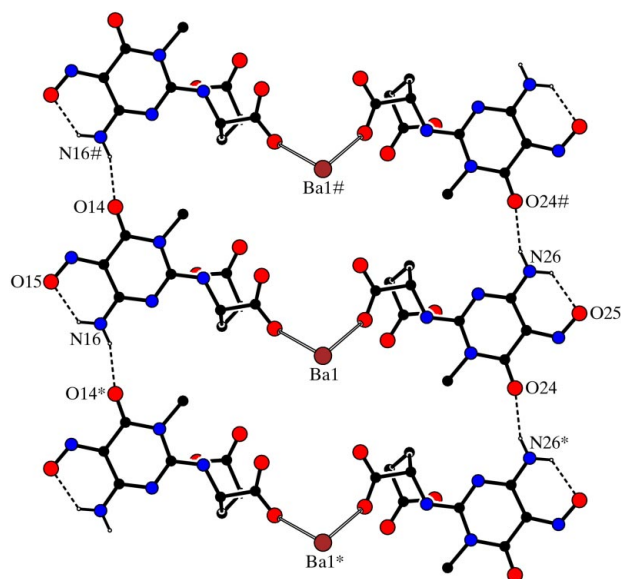

Figure 4
Part of the crystal structure of (I), showing the formation of a molecular ladder along [100]. For the sake of clarity, the water molecules and the H atoms bonded to C and O atoms have been omitted, as has the unit-cell outline. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(x - 1, y, z)$ and $(1 + x, y, z)$, respectively.
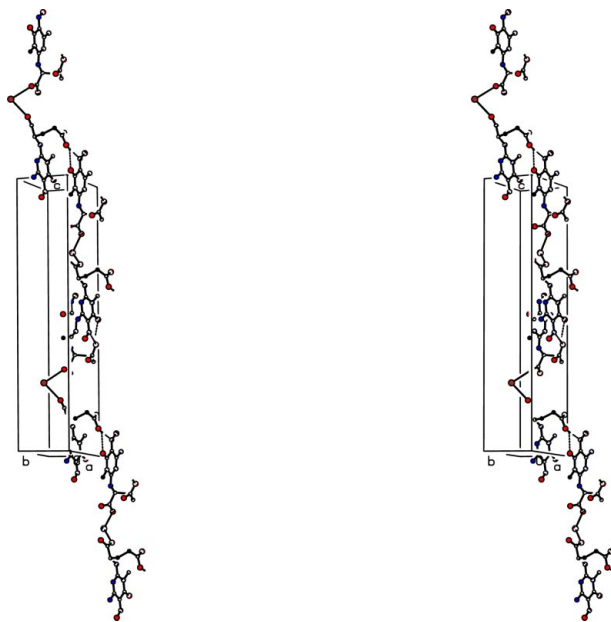

Figure 5
A stereoview of part of the crystal structure of (I), showing the formation of a $C_2^2(34)$ chain along [10$\bar{1}$]. For the sake of clarity, the water molecules and the H atoms bonded to C and N atoms have been omitted.

In the second motif involving the anions, carboxyl atoms O124 and O224 at (x, y, z) act as donors to, respectively, amidic atoms O14 at $(2 - x, y - \frac{1}{2}, -z)$ and O24 at $(1 - x, y - \frac{1}{2}, 1 - z)$, and the combination of these two hydrogen bonds generates a $C_2^2(34)$ chain running parallel to the [10$\bar{1}$] direction (Fig. 5). The combination of [100], [010] and [10$\bar{1}$] chains is sufficient to generate a three-dimensional framework built solely from cations and anions.

It is striking that, despite the occurrence in (I) of both un-ionized carboxyl groups and polarized nitrosyl groups, there are no short O—H···O hydrogen bonds with a carboxyl donor and a nitrosyl acceptor. Such hydrogen bonds are found not only in the corresponding acid, (II) (Arranz Mascarós *et al.*, 2003), but also in the analogous acids derived from glycine, methionine, serine, threonine and valine (Low *et al.*, 2000), in all of which such O—H···O hydrogen bonds have an O···O distance of around 2.50 Å. Instead, the un-ionized carboxyl group in (I) acts as hydrogen-bond donor towards the amidic O atom, while the nitrosyl O atom does not accept any intermolecular hydrogen bonds. In the metal(II) complexes formed by similar ligands based on monocarboxylic amino acids, and therefore lacking free un-ionized carboxyl groups, the only intermolecular hydrogen-bond donors to nitrosyl O atoms are water molecules (Godino Salido *et al.*, 2004).

It may be noted, therefore, that the cations and anions in (I) can generate the framework without any contribution from the hydrogen bonds formed by the water molecules. Those involving atoms O1 and O6 undoubtedly reinforce the framework, but we were unable to locate with any confidence the H atoms bonded to water atoms O2, O3 and O4, although each of these atoms is within hydrogen-bonding distance of at least two other O atoms.

Experimental

Barium chloride dihydrate (0.33 mmol) was added to a solution of *N*-(6-amino-3,4-dihydro-3-methyl-5-nitroso-4-oxopyridin-2-yl)glutamic acid (0.33 mmol) in water (40 ml). Slow evaporation of the resulting solution yielded pink crystals of the title complex, which were collected by filtration and washed with ethanol. Analysis found: C 28.7, H 4.6, N 16.5%; $C_{20}H_{36}BaN_{10}O_{18}$ requires: C 28.5, H 4.3, N 16.6%.

Crystal data

[Ba(C$_{10}$H$_{12}$N$_5$O$_6$)$_2$(H$_2$O)$_6$]	$D_x = 1.805$ Mg m^{-3}
$M_r = 841.92$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 6791
$a = 7.5404$ (2) Å	reflections
$b = 6.5754$ (2) Å	$\theta = 3.1–27.5°$
$c = 31.4285$ (10) Å	$\mu = 1.38$ mm^{-1}
$\beta = 94.6675$ (15)°	$T = 120$ (2) K
$V = 1553.09$ (8) Å^3	Block, colourless
$Z = 2$	$0.30 \times 0.20 \times 0.20$ mm

Data collection

Nonius KappaCCD area-detector diffractometer	6791 independent reflections
φ scans, and ω scans with κ offsets	5620 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)	$R_{int} = 0.063$
	$\theta_{max} = 27.5°$
	$h = -9 \rightarrow 9$
	$k = -8 \rightarrow 8$
$T_{min} = 0.676$, $T_{max} = 0.763$	$l = -39 \rightarrow 40$
15 610 measured reflections	

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.083$
$S = 1.00$
6791 reflections
445 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0321P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.49$ e Å^{-3}
$\Delta\rho_{min} = -0.96$ e Å^{-3}
Absolute structure: Flack (1983), with 2923 Friedel pairs
Flack parameter: −0.034 (14)

Table 1
Selected geometric parameters (Å, °).

N11—C12	1.333 (6)	N21—C22	1.326 (6)
C12—N13	1.380 (6)	C22—N23	1.387 (6)
N13—C14	1.398 (6)	N23—C24	1.388 (6)
C14—C15	1.461 (7)	C24—C25	1.465 (6)
C15—C16	1.453 (7)	C25—C26	1.440 (7)
C16—N11	1.338 (6)	C26—N21	1.340 (6)
C12—N12	1.316 (6)	C22—N22	1.329 (6)
C14—O14	1.223 (6)	C24—O24	1.225 (6)
C15—N15	1.335 (6)	C25—N25	1.328 (6)
N15—O15	1.279 (5)	N25—O25	1.291 (5)
C16—N16	1.312 (6)	C26—N26	1.317 (6)
C122—O121	1.255 (7)	C222—O221	1.256 (6)
C122—O122	1.262 (7)	C222—O222	1.255 (7)
C125—O123	1.213 (6)	C225—O223	1.212 (6)
C125—O124	1.334 (6)	C225—O224	1.320 (6)
Ba1—O1	2.715 (3)	Ba1—O6	2.910 (4)
Ba1—O2	2.777 (4)	Ba1—O121	2.788 (4)
Ba1—O3	2.796 (4)	Ba1—O221	2.881 (3)
Ba1—O4	2.806 (4)	Ba1—O223^i	2.939 (4)
Ba1—O5	2.887 (3)		
N13—C12—N12—C121	−176.7 (4)	N23—C22—N22—C221	−179.6 (4)
C12—N12—C121—C122	−162.3 (5)	C22—N22—C221—C222	−162.3 (4)
N12—C121—C122—O121	−174.2 (5)	N22—C221—C222—O221	−10.6 (7)
C121—C122—O121—Ba1	−141.9 (4)	C221—C222—O221—Ba1	143.9 (4)
C12—N12—C121—C123	74.2 (6)	C22—N22—C221—C223	75.4 (6)
N12—C121—C123—C124	61.8 (6)	N22—C221—C223—C224	61.6 (6)
C121—C123—C124—C125	−61.2 (7)	C221—C223—C224—C225	−63.7 (6)
C123—C124—C125—O123	111.2 (6)	C223—C224—C225—O223	126.0 (6)
C14—C15—N15—O15	176.9 (4)	C24—C25—N25—O25	179.2 (4)

Symmetry code: (i) $x, y + 1, z$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N16—H16$A\cdots$O14^{ii}	0.88	2.04	2.888 (5)	161
N16—H16$B\cdots$O15	0.88	1.98	2.625 (5)	129
N26—H26$A\cdots$O24^{iii}	0.88	2.06	2.892 (5)	159
N26—H26$B\cdots$O25	0.88	1.98	2.629 (5)	129
O124—H124$\cdots$N15^{iv}	0.84	2.10	2.936 (5)	174
O224—H224$\cdots$N25^v	0.84	2.05	2.886 (5)	174
O1—H1$A\cdots$O15^{vi}	0.90	1.95	2.853 (5)	175
O1—H1$B\cdots$O123^{vii}	0.83	1.92	2.743 (6)	169
O5—H5$A\cdots$O122	0.93	1.86	2.709 (5)	151
O5—H5$B\cdots$O222	0.94	1.94	2.746 (5)	142
O6—H6$A\cdots$O122^{ii}	0.81	2.33	2.987 (5)	139
O6—H6$B\cdots$O222^{ii}	1.04	1.94	2.794 (5)	137

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

The systematic absences permitted $P2_1$ and $P2_1/m$ as possible space groups. In view of the enantiopure nature of the starting (S)-glutamic acid, space group $P2_1$ was selected and subsequently confirmed by the analysis. It was consistently found that free refinement caused the Ba atom to edge steadily along the y-axis direction. Accordingly, the y coordinate was fixed at 0.75. The H atoms in the organic ligands were all located from difference maps and then treated as riding atoms with C—H distances of 0.98 (CH₃), 0.99 (CH₂) or 1.00 Å (CH), N—H distances of 0.88 Å and O—H distances of 0.84 Å, and with $U_{iso}(H) = 1.2U_{eq}(C,N)$, or $1.5U_{eq}(C)$ for the methyl groups, and $1.5U_{eq}(O)$. The H atoms bonded to water atoms O1, O5 and O6 were located from difference maps and then allowed to ride at the O—H distances (0.81–1.04 Å) located from the difference maps, with $U_{iso}(H) = 1.2U_{eq}(O)$. No clear indications could be found for the positions of the H atoms bonded to O2, O3 and O4. The absolute configuration was established by means of the Flack (1983) parameter and confirmed the expected S configuration of the glutamic acid fragments.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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