Metal Ion Binding by Amino Acids:
Strontium and Barium L-Aspartate Trihydrate Sr/Ba(L-Asp) · 3 H$_2$O

Hubert Schmidbaur*, Patrizia Mikulcik, and Gerhard Müller

Anorganisch-chemisches Institut der Technischen Universität München,
Lichtenbergstraße 4, D-8046 Garching

Strontium and barium L-aspartate are obtained by neutralization of aqueous solutions of L-aspartic acid with strontium or barium hydroxide, respectively. Slow crystallization from hot water affords the crystalline trihydrates, saturated solutions of which show pH values of 11.0 and 10.8 at ambient temperature. – The crystal structure of the two compounds has been determined by single crystal X-ray diffraction. The compounds are isomorphous (orthorhombic, space group $P2_12_12_1$), and the structural parameters are very similar as expected from the small differences in the ionic radii of the two metals. – The cations are arranged in double strings parallel to the b axis. The L-aspartate dianions are bridging these double strings by chelating contacts of the two carboxylate groups with the metal atoms of different strings to give layers. While the α-carboxylate groups are only bidentate and associated with one metal atom each, the β-carboxylate oxygen atoms are also each bridging two adjacent metals of the neighbouring string. The three water molecules are all coordinated to the metal atoms, which attain coordination number 9. The amino groups are not engaged in metal coordination, but are part of a system of hydrogen bonds cross-linking the layers.

Complexation of the alkali metals by amino acids and proteins plays an important role in many biological processes[1–3]. Evidence suggests that aspartate and glutamate units are among the principal mediators of metal binding. While magnesium and calcium no doubt are the biologically most essential metals, with high concentrations being present in most body fluids, tissues, and bones, the roles of strontium and barium are less obvious[4–6]. Both metals are found as trace elements in biological systems, however, and are known to be antagonists for some of the more common metals (strontium mainly for calcium, and barium for potassium)[7,8]. Barium, the heaviest of the alkaline earth metals, is poisonous already in relatively low doses.

The total contents of strontium in the skeleton of an adult human is estimated to be no less than 0.3 g, but the values for barium are much lower[9]. These data have recently gained renewed relevance in connection with contamination by the radioactive isotopes, particularly ⁹⁰Sr, and drugs based on complexing agents including amino acids have been developed for treatment of strontium "poisoning"[10].

Information on stuctures of the strontium and barium complexes with "natural" ligands is still very limited. A diglycine complex of strontium has been structurally characterized[11], and in the course of work carried out in our laboratory the crystal structure of strontium and barium L-glutamate hexahydrates have been determined[12].

As an extension of these studies we now report on the preparation of the analogous L-aspartate complexes of the two heavy alkaline earth metals. In a series of related investigations the structures of coordination compounds with L-aspartate and L-glutamate anions as ligands for lithium[13], potassium[13], magnesium[12,14,15], calcium[16], zinc[17], and manganese(II)[18] have already been presented. It is expected that a consistent picture of metal ion binding by the two most important acidic amino acids (L-Asp and L-Glu) will emerge as the studies become more detailed and more comprehensive. This knowledge is important since metal ion transport in body fluids and through membranes, as well as metal deposition, storage, and mobilization, will depend at least in part on the relative complexing ability of these ubiquitous amino acids and their peptides.

Results and Discussion

Preparation and Stoichiometry

Neutralization of aqueous solutions of L-aspartic acid (L-AspH$_2$) by equivalent quantities of strontium or barium hydroxide at elevated temperature affords solutions from which the title compounds (the *tri*hydrates) can be crystallized on cooling.

$$\text{L-AspH}_2 + \text{M(OH)}_2 \rightarrow \text{M(L-Asp)} + 2 \text{ H}_2\text{O}$$
$$(\text{M} = \text{Sr, Ba})$$
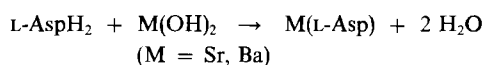
The trihydrates show alkaline reaction (pH 11.0 and 10.8, resp.) when dissolved in pure water owing to partial hydrolysis, but no precipitates appear.

The stoichiometry agrees with the results obtained for the analogous system Ca(OH)$_2$/L-AspH$_2$ with the exception that a *tetra*hydrate Ca(L-Asp) · 4 H$_2$O is found to crystallize from solutions of the calcium salt (monoclinic, space group $C2$). [A *di*hydrate Ca(L-Asp) · 2 H$_2$O is also available (orthorhombic $P2_12_12_1$), but can only be obtained by treatment of a calcium hydrogen L-aspartate chloride precursor with KOH.]

By contrast, the corresponding magnesium compound, the *tri*hydrate Mg(L-Asp) · 3 H$_2$O (orthorhombic, space group $P2_12_12_1$) can only be obtained from the reaction of magnesium hydrogen L-aspartate (or hydrogen L-aspartate chloride) with concentrated KOH solutions.

The experimental conditions employed for the related L-glutamates are similar. Again, the strontium and barium salts are available by simple neutralization reactions of L-glutamic acid (L-GluH$_2$) with the metal hydroxides, while the magnesium and calcium salts require the use of a stronger base. The magnesium salt crystallizes as the *te-*trahydrate, the calcium salt as the *tri*hydrate, and the (iso-morphous) strontium and barium salts as *hexa*hydrates. All of these L-glutamates crystallize orthorhombically in the space group $P2_12_12_1$.

The methods for the preparation to be followed for the alkaline earth L-aspartate and L-glutamate complexes thus directly reflect the increase in basicity of the metal hydroxides. The number of hydrate water molecules, however, shows no consistent pattern, and is certainly not directly related to the increase of the cation radius within Group II, but appears to be influenced by a number of other factors.

Crystal Structures

The crystals of Sr(L-Asp) · 3 H$_2$O and Ba(L-Asp) · 3 H$_2$O are isomorphous. The unit cells of the orthorhombic crystals (space group $P2_12_12_1$) show only minor differences, obviously due to the different cation radii of strontium and barium (Table 1).

In the crystals, the metal atoms are arranged in double strings running parallel to the *b* axis. They are nine-coordinate exclusively to oxygen atoms of the carboxylate groups of the anions and of the water molecules. The amino groups have no metal contacts. The environment of the Sr/Ba atoms is shown in Figure 1, the coordination of the Asp^{2-} anion in Figure 3. As a combination of these two connectivity patterns, a layer structure is obtained as shown in Figure 2. These layers are connected by a system of hydrogen bonds mainly involving water/carboxylate and water/amino group contacts (Table 2).
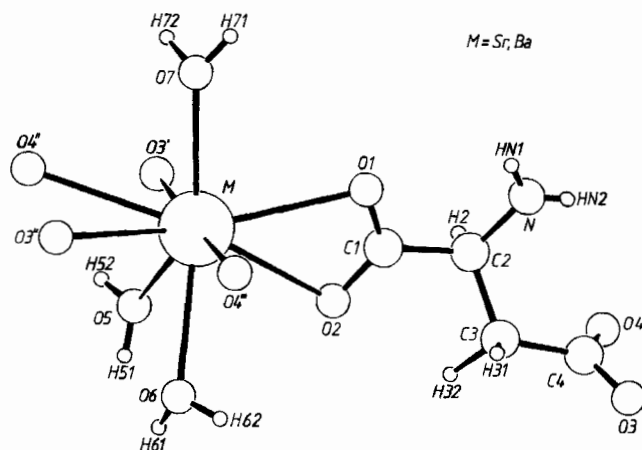
Table 1. Selected distances [Å] and angles [°] in the structures of Sr(L-Asp) · 3 H$_2$O and Ba(L-Asp) · 3 H$_2$O (see figures for atomic numbering)

Distances

Sr	-O1	2.713(4)	Sr	-O2	2.707(5)
Sr	-O3'	2.666(6)	Sr	-O3''	2.635(8)
Sr	-O4'	2.799(7)	Sr	-O4'''	2.580(7)
Sr	-O5	2.568(8)	Sr	-O6	2.683(7)
Sr	-O7	2.627(3)	O1	-C1	1.258(7)
O2	-C1	1.254(7)	C1	-C2	1.540(8)
C2	-C3	1.510(9)	C3	-C4	1.522(7)
O3	-C4	1.29(1)	O4	-C4	1.23(1)

Angles

O1	-Sr-O2	48.0(1)	O1	-Sr-O3'	84.2(2)
O2	-Sr-O3'	88.5(2)	O3''-Sr-O3'		112.4(2)
O4''-Sr-O3'		65.4(2)	O5	-Sr-O3'	70.3(2)
O6	-Sr-O3'	140.5(2)	O3'	-Sr-O4'''	152.7(2)
O3'	-Sr-O7	73.3(2)	O1	-Sr-O3''	146.9(2)
O2	-Sr-O3''	152.6(2)	O3''-Sr-O4''		48.1(1)
O3''-Sr-O5		97.1(2)	O3''-Sr-O6		78.0(2)
O3''-Sr-O7		80.8(2)	O1	-Sr-O4''	144.2(2)
O2	-Sr-O4''	141.9(2)	O4''-Sr-O5		72.6(2)
O4''-Sr-O6		107.6(2)	O4''-Sr-O7		76.6(2)
O1	-Sr-O4'''	83.3(2)	O2	-Sr-O4'''	100.8(2)
O3'	-Sr-O4'''	152.7(2)	O3''-Sr-O4'''		69.0(2)
O4''-Sr-O4'''		115.2(2)	O5	-Sr-O4'''	137.0(2)
O6	-Sr-O4'''	66.6(2)	O7	-Sr-O4'''	80.3(2)
O1	-Sr-O6	107.9(2)	O2	-Sr-O6	74.6(2)
O5	-Sr-O6	70.7(1)	O1	-Sr-O7	76.9(1)
O1	-Sr-O5	115.7(2)	O2	-Sr-O5	72.7(2)
O2	-Sr-O7	123.7(1)	O5	-Sr-O7	139.5(2)
O6	-Sr-O7	145.4(2)	O1	-C1-O2	122.5(5)
O1	-C1-C2	118.2(5)	O2	-C1-C2	119.1(5)
N	-C2-C1	116.3(5)	N	-C2-C3	111.4(6)
C1	-C2-C3	109.9(5)	C2	-C3-C4	115.2(6)
O3	-C4-O4	123.8(5)	O3	-C4-C3	117(1)
O4	-C4-C3	119(1)			

Distances

Ba	-O1	2.880(2)	Ba	-O2	2.868(2)
Ba	-O3'	2.771(2)	Ba	-O3''	2.776(3)
Ba	-O4''	2.939(2)	Ba	-O4'''	2.744(2)
Ba	-O5	2.768(3)	Ba	-O6	2.832(3)
Ba	-O7	2.809(2)	O1	-C1	1.261(3)
O2	-C1	1.249(4)	C1	-C2	1.537(4)
C2	-C3	1.509(5)	C3	-C4	1.522(4)
O3	-C4	1.263(4)	O4	-C4	1.246(4)

Angles

O1	-Ba-O2	45.1(1)	O1	-Ba-O3'	83.6(1)
O2	-Ba-O3'	89.6(1)	O3''-Ba-O3'		111.8(1)
O4''-Ba-O3'		67.2(1)	O5	-Ba-O3'	69.8(1)
O6	-Ba-O3'	140.5(1)	O3'	-Ba-O4'''	154.1(1)
O3'	-Ba-O7	73.4(1)	O1	-Ba-O3''	149.4(1)
O2	-Ba-O3''	152.7(1)	O3''-Ba-O4''		45.4(1)
O3''-Ba-O5		96.9(1)	O3''-Ba-O6		75.9(1)
O3''-Ba-O7		79.5(1)	O1	-Ba-O4''	145.5(1)
O2	-Ba-O4''	145.7(1)	O4''-Ba-O5		74.3(1)
O4''-Ba-O6		104.6(1)	O4''-Ba-O7		74.4(1)
O1	-Ba-O4'''	84.9(1)	O2	-Ba-O4'''	98.4(1)
O3'	-Ba-O4'''	154.1(1)	O3''-Ba-O4'''		69.9(1)
O4''-Ba-O4'''		113.5(1)	O5	-Ba-O4'''	136.1(1)
O6	-Ba-O4'''	65.4(1)	O7	-Ba-O4'''	81.9(1)
O1	-Ba-O6	109.6(1)	O2	-Ba-O6	76.8(1)
O5	-Ba-O6	70.8(1)	O1	-Ba-O7	80.1(1)
O1	-Ba-O5	113.4(1)	O2	-Ba-O5	74.0(1)
O2	-Ba-O7	124.5(1)	O5	-Ba-O7	138.5(1)
O6	-Ba-O7	144.1(1)	O1	-C1-O2	122.8(3)
O1	-C1-C2	118.0(3)	O2	-C1-C2	119.2(3)
N	-C2-C1	115.2(3)	N	-C2-C3	111.2(3)
C1	-C2-C3	109.0(3)	C2	-C3-C4	116.2(3)
O3	-C4-O4	123.5(2)	O3	-C4-C3	116.5(3)
O4	-C4-C3	119.9(3)			

Figure 1. Inner coordination sphere of the metal atoms in the structures of Sr/Ba(L-Asp) · 3 H$_2$O (arbitrary radii for clarity)

Each of the crystallographically equivalent metal atoms is chelated by an α- and a β-carboxylate group (of two different, but again crystallographically equivalent amino acids: O1/O2 and O3''/O4'' in Figure 3). The β-carboxylate groups are not only chelating, however, but each of its oxygen atoms is also in a bridging position between two adjacent metals. No such ambidentate function applies to the α-carboxylate groups. Based on the different functionality, the α-carboxylate groups are more symmetrically coordinated to the metal than the β-carboxylate groups (Table 1).
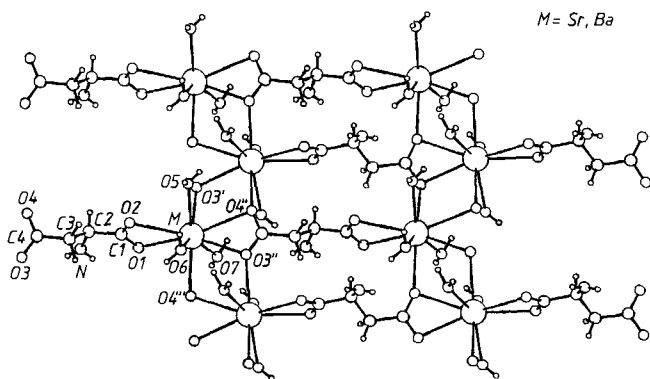
Figure 2. The layer structure of Sr/Ba(L-Asp) · 3 H₂O (arbitrary radii, hydrogen bonds omitted for clarity)
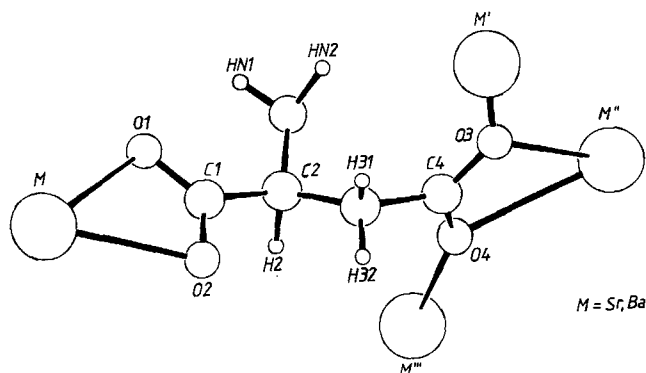

Figure 3. Metal coordination of the L-Asp unit in the structures of Sr/Ba(L-Asp) · 3 H₂O (arbitrary radii for clarity)

Table 2. Hydrogen bonds (A−B···C) [Å] in the structures of a) Sr(L-Asp) · 3 H₂O, b) Ba(L-Asp) · 3 H₂O

A — B ··· C	A — B	B ··· C	A ──── C	Sym.op.
a) O5-H51 ···O1	0.979(9)	1.995(4)	2.797(9)	a
O5-H52 ···O7	0.910(7)	2.369(7)	2.838(9)	b
O6-H61 ···O1	0.870(6)	2.052(4)	2.838(8)	a
O6-H62 ···N	0.894(8)	1.981(6)	2.812(9)	c
O7-H71 ···O2	0.893(3)	1.932(4)	2.812(5)	d
O7-H72 ···O6	1.073(6)	1.888(6)	2.855(8)	b
b) O5-H51 ···O1	0.836(3)	1.990(2)	2.776(3)	a
O5-H52 ···O7	0.781(3)	2.087(2)	2.862(4)	b
O6-H61 ···O1	0.878(3)	1.981(2)	2.834(3)	a
O6-H62 ···N	0.839(3)	2.010(3)	2.837(4)	c
O7-H71 ···O2	0.875(2)	1.916(2)	2.779(3)	d
O7-H72 ···O6	0.931(2)	1.951(3)	2.814(3)	b

Symmetry operations :
a: 0.5-x,-y,0.5+z ; b: x-0.5,0.5-y,-z ;
c: 0.5+x,-y-0.5,-z; d: 0.5-x,-y,z-0.5

Since all three of the water molecules indicated by the stoichiometry are attached directly to metal centers, the lattices contain no "interstitial" hydrate water molecules. This is important to note, since in the structures of the related L-glutamates Sr/Ba(L-Glu) · 6 H₂O three of the six water molecules are present as interstitial, hydrogen-bonded water. Otherwise, however, the structures of the L-aspartate and L-glutamates are very similar. The cation-anion connectivity

pattern in particular is virtually identical: The geometry of metal coordination is almost superimposable, and the ligand role of the amino acid is following the same principle. It appears that the lengthening of the amino acid chain by one CH₂ group on going from L-aspartate to L-glutamate simply gives rise to a little more room between the organic "spacers" holding the double chains of metals apart, which is filled with extra water molecules.

Not surprisingly, a comparison of structural details of the two L-aspartate complexes (distances and angles in Table 1) shows consistently the variations resulting from the differences in the cation radii of strontium and barium. The average difference in the distances in the first coordination sphere of Sr/Ba can be calculated as 0.157 Å, in fair agreement with tabulated standard values (0.160 Å)[19].

The O−M−O angles are more similar and seem to be virtually independent of the relative size of the metal (Table 1).

The present work leads to a few interesting conclusions:

1) For the coordinatively non-discriminative large alkaline earth metals strontium and barium a very high coordination number (9) and somewhat flexible coordination geometries are found, which are basically the same for both metals and for L-aspartic and L-glutamic acid ligands. This flexibility allows e. g. the accommodation of interstitial water molecules without any major changes at the metal sites or in the connectivity pattern.

2) Concerning the related calcium L-aspartates and L-glutamates the change in amino acid (L-Asp/L-Glu) leads to more severe alterations in the overall structure and in the coordination of the metal, where more than one coordination number can be realized[6−8].

3) Concerning magnesium, the influence of the metal is very pronounced and a strict adherance to coordination number 6 and a rigid octahedral geometry are observed[20]. Changes in the amino acid ligand induce fundamental changes in the crystal structure.

4) Nitrogen coordination and chelation by more than one carboxylate group play either no (Sr, Ba) or a relatively insignificant role (Ca) for the heavy elements, but are very important for magnesium.

Experimental

Strontium L-Aspartate Trihydrate, Sr(L-Asp) · 3 H₂O: L-Aspartic acid (2.875 g, 22 mmol) is dissolved in 90 ml of hot water (90°C) and treated with strontium dihydroxide octahydrate (5.85 g, 22 mmol). The reaction mixture is heated to reflux for 3 h and filtered while hot from any insoluble material. The filtrate is then allowed to cool to room temp. over the period of 72 h. Colorless crystals are formed, which give an analysis corresponding to the trihydrate.

No melting is observed below 330°C. Aqueous solutions show a pH of 11.0.

$C_4H_{11}NO_7Sr$ (270.6)   Calcd. C 17.75 H 4.10 N 5.18
Found C 17.58 H 4.05 N 5.06

Barium L-Aspartate Trihydrate, Ba(L-Asp) · 3 H_2O: The barium compound is obtained similarly from 3.33 g (25 mmol) of L-AspH$_2$ and 7.89 g (25 mmol) of Ba(OH)$_2$ · 8 H_2O. The compound crystallizes as colorless needles, dec. 279°C. Aqueous solutions show a pH of 10.8. — ^{13}C NMR (D$_2$O; δ values rel. int. dioxane, converted to TMS; 80°C): δ = 41.0, CH$_2$; 52.77, CH; 178.8 and 179.9, CO$_2$.

$C_4H_{11}BaNO_7$ (322.5)   Calcd. C 14.90 H 3.43 N 4.34
Found C 14.93 H 3.48 N 4.36

Determination of the Crystal Structures: Suitable crystals of Sr(L-Asp) · 3 H_2O and Ba(L-Asp) · 3 H_2O obtained from hot concentrated aqueous solutions on cooling were sealed into glass capillaries and investigated directly on a diffractometer. The crystal data and details of the structure elucidation procedure are given below. The data were corrected for Lp effects and for absorption. The structures were solved by direct methods (SHELXS-86) and completed by Fourier syntheses. All H atoms could be located in difference syntheses and were included in the final refinement cycles using isotropic displacement parameters (SHELX-76). The absolute configuration determined by the amino acid was confirmed by refinement of the inverse data set, which gave a significantly higher R value [R(wR) = 0.049 (0.046) for Sr, 0.027 (0.026) for Ba].

Table 3 shows the atomic coordinates, Table 1 gives selected distances and angles, and Table 2 a list of hydrogen bonds in the crystal. Complete lists of coordinates have been deposited[21].

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters for Sr(L-Asp) · 3 H_2O and Ba(L-Asp) · 3 H_2O

ATOM	X/A	Y/B	Z/C	U(eq.)
SR	0.2512(2)	0.12343(6)	0.01532(3)	0.022
O1	0.247(1)	−0.1101(4)	−0.1041(3)	0.046
O2	0.1977(6)	−0.1361(5)	0.0783(3)	0.039
O3	0.3983(9)	−0.6359(8)	0.0410(7)	0.049
O4	0.0957(9)	−0.6194(7)	0.0327(7)	0.040
O5	0.0536(9)	0.1264(7)	0.1947(8)	0.059
O6	0.4661(8)	0.0865(7)	0.1965(7)	0.033
O7	0.238(1)	0.2068(4)	−0.1951(3)	0.039
N	0.230(2)	−0.3876(5)	−0.1511(3)	0.037
C1	0.2138(9)	−0.1831(6)	−0.0196(5)	0.038
C2	0.1785(9)	−0.3343(6)	−0.0395(5)	0.036
C3	0.263(2)	−0.4160(6)	0.0549(5)	0.046
C4	0.248(2)	−0.5682(5)	0.0416(4)	0.034
BA	0.25518(2)	0.11995(1)	0.01364(1)	0.027
O1	0.2436(3)	−0.1229(2)	−0.1074(2)	0.044
O2	0.2097(4)	−0.1495(2)	0.0733(2)	0.051
O3	0.4008(3)	−0.6334(3)	0.0435(3)	0.066
O4	0.1106(3)	−0.6142(2)	0.0318(3)	0.055
O5	0.0472(4)	0.1195(4)	0.2030(2)	0.087
O6	0.4747(3)	0.0918(3)	0.2029(2)	0.047
O7	0.2411(4)	0.2163(2)	−0.2049(2)	0.051
N	0.2149(6)	−0.3865(3)	−0.1549(3)	0.056
C1	0.2157(4)	−0.1938(3)	−0.0234(3)	0.040
C2	0.1807(4)	−0.3401(3)	−0.0426(3)	0.039
C3	0.2839(5)	−0.4181(3)	0.0419(4)	0.077
C4	0.2615(5)	−0.5659(2)	0.0370(3)	0.037

Crystal Structure Data of Sr(L-Asp) · 3 H_2O: $C_4H_{11}NO_7Sr$, M_r = 272.755; crystal size: 0.15 · 0.08 · 0.35 mm^3; orthorhombic, $P2_12_12_1$ (No. 19); a = 7.304(1), b = 9.914(1), c = 11.837(1) Å; V = 857.1 Å^3; Z = 4; d_{calcd} = 2.113 g/cm^3; $\mu(Mo-K_\alpha)$ = 61.1 cm^{-1}; $F(000)$ = 544 e; T = 23°C; Enraf-Nonius CAD4 diffractometer; Mo-K_α radiation, λ = 0.71069 Å; graphite monochromator; scan: Θ − 2Θ; scan width (in Δω): 0.9 + 0.35 tanΘ; (sinΘ/λ)$_{max}$ 0.638; hkl range +10, +13, ±16; measured reflections 2121; unique reflections 1855; R_{int} = 0.017; refined parameters 118; observed reflections 1383 [$F_o \geq 4.0 \cdot \sigma(F_o)$]; R = 0.035, R_w = 0.031; R = $\Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; R_w = $[\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$, w = $1/\sigma^2(F_o)$, function minimized: $\Sigma w(|F_o| - |F_c|)^2$. Δϱ$_{fin}$ (max/min) = 2.15/−1.50 e/Å^3 (close to Sr at 0.97 Å).

Crystal Structure Data of Ba(L-Asp) · 3 H_2O: $C_4H_{11}BaNO_7$, M_r = 322.475; crystal size: 0.11 · 0.24 · 0.35 mm^3; orthorhombic, $P2_12_12_1$ (No. 19); a = 7.564(1); b = 10.227(1); c = 12.024(1) Å; V = 930.1 Å^3; Z = 4; d_{calcd} = 2.303 g/cm^3; $\mu(Mo-K_\alpha)$ = 42.8 cm^{-1}; $F(000)$ = 616 e; T = 23°C; Enraf-Nonius CAD4 diffractometer; Mo-K_α radiation, λ = 0.71069 Å; graphite monochromator; scanΘ − 2Θ; scan width (in Δω): 0.9 + 0.35 tanΘ; (sinΘ/λ)$_{max}$ 0.659; hkl range +10, ±13, 15; measured reflections 2499; unique reflections 2222; R_{int} = 0.01; refined parameters 122; observed reflections 2182 [$F_o \geq 4.0 \cdot \sigma(F_o)$]; R = 0.016, R_w = 0.021 (definitions as above); Δϱ$_{fin}$ (max/min) = 0.70/−0.85 e/Å^3.

CAS Registry Numbers

Sr(L-Asp) · 3 H_2O (CC entry): 127357-25-9 / Sr(L-Asp) · 3 H_2O (salt entry): 127357-26-0 / Ba(L-Asp) · 3 H_2O (CC entry): 127357-27-1 / Ba(L-Asp) · 3 H_2O (salt entry): 127357-28-2

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[21] Further details and basic data concerning the X-ray analysis may be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2 (W. Germany), by specifying registry number CSD-54412, author, and the reference to this publication.

[31/90]