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Zinc and lithium hydrogen-β-glutamate: large-pore network layer structures

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The symmetrical anion [β-GluH]$^-$ of β-glutamic acid [β-GluH$_2$] has been introduced into crystal engineering of metal complexes for the first time. Neutralization of aqueous solutions of β-glutamic acid with zinc oxide or lithium hydroxide affords crystalline samples of zinc bis(hydrogen-β-glutamate) trihydrate and lithium hydrogen-β-glutamate hydrate, respectively. [Zn(β-GluH)$_2$(H$_2$O)$_3$] has a layer structure with corrugated sheets featuring a square-grid pattern of the tetra-coordinated zinc dications and bridging [O$_2$C–CH$_2$CH(NH$_3$)CH$_2$–CO$_2$]$^-$ anions (in their *gauche*-conformation). The uniform meshes of the network are based on puckered 32-membered rings. Neighbouring undulated layers are mutually shifted into a space-filling indentation which also generates a network of hydrogen bonds involving the ammonio and carboxylate groups and the intercalated water molecules. [Li(β-GluH)(H$_2$O)] has a less corrugated layer structure based on a parallelogram-grid of lithium cations which are connected by three bridging [β-GluH]$^-$ anions (in their *anti*-conformation). The water molecule is part of the tetrahedral coordination sphere of the metal atom. The layers represent a mixed-mesh network with pores based on 8- and 32-membered rings. Neighbouring layers are mutually shifted to allow for extensive hydrogen bonding.

Introduction

α-Aspartic and α-glutamic acid are of prime importance as constituents of small and large proteins. Apart from their relevance to the determination of the fundamental structure and the folding of proteins, these two amino-bis(carboxylic) acids offer their extra carboxylate functions for the binding of metal cations. This capability is the basis for the role of proteins – or protein regions rich in α-aspartate and α-glutamate – in biomineralization.[1] It also is essential for the effectiveness of many metal cofactors in enzymes.[2]

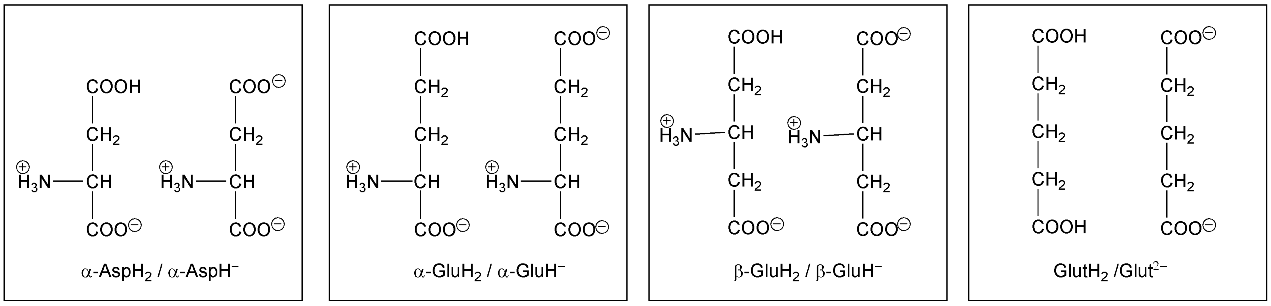
Depending on the pH of the aqueous solutions, the two acids and their anions are able to form a variety of complexes with base and trace metals either through mono-, di- or tri-dentate coordination.[3] The asymmetric position of the amino group between the two terminal carboxylate groups allows for a functional flexibility through the formation of different chelate ring sizes (Scheme 1).

These aspects have led to extensive studies of the coordination chemistry of the two amino acids, mainly in their "natural" enantiomeric form (L), with alkali and alkaline earth metals, in particular Li, Na, K, Mg, and Ca.[3] Moreover, metal L-α-aspartates and L-α-glutamates are widely used as food additives and are important chemotherapeutic agents,[3,4] to mention just a few of their most common usages.

By contrast, β-glutamic acid and its metal salts received almost no attention because of their extremely low abundance in biological systems.[5–7] Quite generally, research interest has focussed on β-amino acid chemistry only very recently. In pioneering investigations, β-amino acids were first introduced as new building blocks for the design of novel structural motifs in "β-peptides" and related biooligomers.[8] However, the *coordination chemistry* of β-amino acids is still in its infancy and the number of contributions to this field is very limited.[9]

It should be pointed out that α-aspartic acid may be viewed also as a β-amino acid referring to the position of the amino group relative to the second carboxylate function. However, particularly in peptide chemistry, aspartic acid almost always acts as a standard α-amino acid, and this is also true for metal complexation.[3] While α-/β-aspartic acid is chiral, with a distinct preference for the L-enantiomer in nature, β-glutamic acid is a non-chiral, symmetrical amino acid owing to the position of the amino group on the mirror plane of the molecule in an idealized conformation (Scheme 1).

Following our earlier studies on metal complexation by α-/β-aspartatic and α-glutamic acid[10–15] we have now initiated a program in which β-amino acids and their anions are tested as novel ligands to biorelevant metals.[16,17] The present report illustrates the role of hydrogen-β-glutamate anions as building units in two-dimensional complexes of lithium and zinc.


α-AspH$_2$ / α-AspH$^-$
α-GluH$_2$ / α-GluH$^-$
β-GluH$_2$ / β-GluH$^-$
GlutH$_2$ /Glut^{2-}

Scheme 1 α-Aspartic, α-glutamic, β-glutamic and glutaric acid (α-AspH$_2$, α-GluH$_2$, β-GluH$_2$ and GlutH$_2$) in their neutral/zwitterionic and bis(carboxylate) forms. In contrast to the amino dicarboxylate anions, glutarate is a dianion.

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Experimental

General

All experiments were carried out in bidistilled water and under a nitrogen atmosphere to exclude carbon dioxide. β-Glutamic acid (Sigma Chemical Company) and all other reagents are commercially available. Standard equipment was used throughout.

Zinc bis(hydrogen-β-glutamate) hydrates [zinc bis(β-ammonioglutarate) hydrates, zinc bis(3-ammoniopentane-1,5-dioate) hydrates] $Zn(\beta\text{-}GluH)_2(H_2O)_n$ (n = 1, 3)

A suspension of β-glutamic acid (β-amino-glutaric acid, 147.1 mg, 10 mmol) in 10 mL of water is treated with zinc oxide (40.7 mg, 5 mmol) for 2 h with stirring at room temperature. The reaction mixture is then heated to reflux temperature for 30 min and subsequently cooled to 20 °C. A microcrystalline product is obtained in quantitative yield (as the monohydrate) by removing the solvent completely in a vacuum. Elemental analysis calcd. for $Zn(\beta\text{-}GluH)_2(H_2O)$ ($C_{10}H_{18}N_2O_9Zn$) C 31.97, H 4.83, N 7.46, O 38.33, Zn 17.41; found C 31.98, H 4.83, N 7.44, O 37.95, Zn 17.80%. IR (KBr, cm^{-1}): 3409, s, ν(OH); 3152, s, ν(NH), ν(CH); 2362, w, $\delta_{overtone}(NH_3)$; 1610, s, $\delta(H_2O)$; 1399, s, $\nu(CO_2)$; 1299, m, δ(CH); 1087, w, ν(CN); 724, w, $\gamma(CH_2)$.

For the growth of single crystals of the trihydrate the volume of the solution is reduced to 0.5 mL in a vacuum and carefully layered with methanol (5 mL). The vessel is set aside for 4 weeks at 20 °C (10 mg, 0.6% yield). The CI mass spectra of the two hydrates show only fragments of glutamic acid and its condensation products at m/z 174.2 (8.5%), 156.0 (19.4%), 112.0 (100%) and 104.0 (3.2%).

Lithium hydogen-β-glutamate hydrates [lithium β-ammonioglutarate hydrates, lithium 3-ammoniopentane-1,5-dioate hydrates] $Li(\beta\text{-}GluH)(H_2O)_n$ (n = 1, x)

β-Glutamic acid (73.6 mg, 0.5 mmol) is dissolved in an aqueous solution (5 mL) of lithium hydroxide (12.0 mg, 0.5 mmol) at room temperature (5 min). This solution is concentrated to a volume of 1 mL in a vacuum and set aside for crystallization. After 6 weeks colourless crystals of the monohydrate are collected, 70.4 mg (82% yield). Elemental analysis calcd. for $Li(\beta\text{-}GluH)(H_2O)$ $C_5H_{10}LiNO_5$ C 35.10, H 5.85, N 8.19, Li 4.09; found C 34.83, H 5.81, N 8.08, Li 3.90%. IR (KBr, after drying the sample in a vacuum, cm^{-1}): 3350, s, ν(OH); 3150, s, ν(NH), ν(CH); 2344, w, $\delta_{overtone}(NH_3)$; 1628, s, $\delta(H_2O)$; 1431, s, $\nu(CO_2)$; 1291, m, δ(CH); 1102, m, ν(CN); 657, s, $\gamma(CH_2)$.

Single crystal X-ray diffraction analyses

The crystalline samples were placed in an inert oil, mounted on a glass pin and transferred to the cold gas stream of the diffractometer. Crystal data were collected and integrated with an Enraf-Nonius DIP-2020 image plate system (Silicon-Graphics 02 workstation) with monochromated Mo-K_α (λ = 0.71073 Å) radiation at −130 °C. The structures were solved by direct methods using SHELXS-97[18a] and refined by full-matrix least-squares calculations on F^2 with SHELXL-97.[18b] Non-H-atoms were refined with anisotropic thermal parameters. H-Atoms were located and refined with isotropic contributions. No extinction corrections were applied. A summary of the crystal data, experimental details and refinement results is listed in Table 1.

CCDC reference numbers 186989 and 186990.

See http://www.rsc.org/suppdata/dt/b2/b205327f/ for crystallographic data in CIF or other electronic format.

Table 1 Summary of crystal data for zinc bis(hydrogen-β-glutamate) trihydrate and lithium hydrogen-β-glutamate hydrate

Empirical formula	$C_{10}H_{22}N_2O_{11}Zn$	$C_5H_{10}LiNO_5$
Formula weight	411.67	171.08
T/°C	−130(2)	−130(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a/Å	8.8510(1)	7.3350(2)
b/Å	9.1050(1)	10.3040(2)
c/Å	19.8280(4)	9.7550(2)
β/°	97.3830(6)	97.141(1)
U/Å^3	1584.66(4)	731.56(3)
Z	4	4
D_c/Mg m^{-3}	1.726	1.553
No. of refl. collected	42910	18561
No. of refl. unique	3514	1619
No. of parameters	305	149
R_{int}	0.040	0.039
μ(Mo-K_α)/mm^{-1}	1.612	0.136
$R1$, $wR2$ (all data)	0.0380, 0.0934	0.0359, 0.0909
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0354, 0.0911	0.0339, 0.0891
ρ/e Å^{-3}	0.922/−0.561	0.249/−0.266

Results

Preparation

The two title compounds can be prepared by neutralization of β-glutamic acid (β-amino-glutaric acid, 3-aminopentane-1,5-dioic acid, $\beta\text{-}GluH_2$) with zinc oxide and lithium hydroxide, respectively, in aqueous solution. Neutralized β-glutamic acid solutions (pH 5.5–8.5) are known to contain the hydrogen-β-glutamate anion $[\beta\text{-}GluH]^-$ as the dominant species.[16] With the remaining acidic proton residing at the nitrogen atom, this anion has – as already pointed out – an ammonio-dicarboxylate structure with (non-chiral) idealized mirror symmetry. Contrary to the hydrogen-α-glutamate anion $[D/L\text{-}\alpha\text{-}GluH]^-$, for $[\beta\text{-}GluH]^-$ no enantiomeric anions are to be considered. Regarding the stoichiometry it should be noted that introduction of this ammonio center reduces the charge of the glutarate(2−) dianion to the charge of a $[\beta\text{-}GluH]^-$ monoanion with a symmetrical charge distribution [− + −].

On complete evaporation of the water solvent from the zinc complex at 20 °C, a monohydrate $[Zn(\beta\text{-}GluH)_2(H_2O)]$ remains in virtually quantitative yield, while by careful crystallization from a water/methanol two-phase system a trihydrate $[Zn(\beta\text{-}GluH)_2(H_2O)_3]$ is obtained. Even after a few weeks only a few crystals can be collected (less than 1% yield).

$[Li(\beta\text{-}GluH)H_2O]$ crystallizes from concentrated aqueous solutions at room temperature in high yield. The monohydrate does not loose water at room temperature in a vacuum as shown by elemental analysis and IR spectroscopy.

Crystal structures

Zinc bis(hydrogen-β-glutamate) trihydrate. Crystals of $[Zn(\beta\text{-}GluH)_2(H_2O)_3]$ are monoclinic, space group $P2_1/n$, with Z = 4 formula units in the unit cell. The asymmetric unit contains one zinc dication, two hydrogen-β-glutamate anions and three water molecules. The $[\beta\text{-}GluH]^-$ anions are in their *gauche*-conformation (Fig. 1).

The metal dications and the hydrogen-β-glutamate anions form a layer structure with the zinc atoms connecting four anions through Zn–O coordinative bonds in a quasi-tetrahedral orientation. Each $[\beta\text{-} GluH]^-$ anion is thus spanning two zinc atoms, and the water molecules are not part of the first coordination sphere of the metal atoms.

The projection onto the layer (Fig. 2) shows the stoichiometric units to form an almost square-grid motif with the zinc atoms in a common plane. The "squares" of zinc atoms are in fact rectangles with edges (metal-to-metal) of 8.851 and 9.105 Å (and all Zn–Zn–Zn angles at 90° by symmetry).

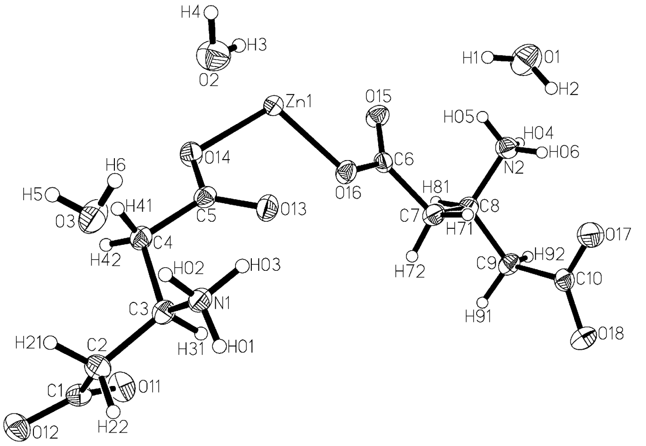

Fig. 1 Asymmetric unit in the structure of Zn(β-GluH)$_2$(H$_2$O)$_3$ with atomic numbering (ORTEP[18c] drawing with 50% probability ellipsoids). Selected bond lengths [Å], angles [°] and symmetry transformations: Zn(1)–O(14) 2.006(1), Zn(1)–O(16) 1.974(1), Zn(1)–O(18)^1 1.966(2), Zn(1)–O(12)^2 1.971(2); O(16)–Zn(1)–O(14) 109.47(6), O(12)^2–Zn(1)–O(14) 98.63(6), O(18)^1–Zn(1)–O(14) 94.49(6), O(12)^2–Zn(1)–O(16) 112.86(7), O(18)^1–Zn(1)–O(16) 113.42(6), O(18)^1–Zn(1)–O(12)^2 123.77(7);1 $x, y - 1, y, z$; 2 $x + 1, y, z$.

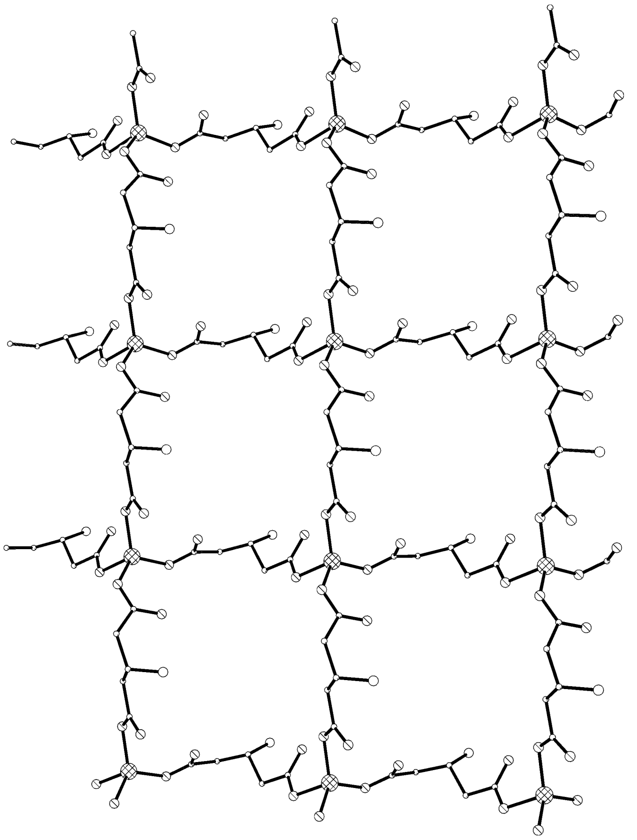

Fig. 2 Projection onto a single layer in the crystalline phase of Zn(β-GluH)$_2$(H$_2$O)$_3$. Water molecules are omitted for clarity.

A projection parallel to this plane along an edge of the rectangle reveals that the layers are strongly corrugated. Two of the four anions at a given zinc atom form loops above and the other two below the reference plane thus conserving a quasi-tetrahedral orientation of the Zn–O valencies. However, the four Zn–O distances are in the range 1.966(2)–2.006(1) Å and the six O–Zn–O angles are in the range 94.49(6)–123.77(7)° indicating quite severe distortions.

In the stacking of the layers, the zinc atom of a given sheet is placed above the center of a rectangle of the following sheet. This packing leads to an efficient filling of space through an intimate indentation (Fig. 3, 4). The ammonio groups appear at the culmination of the ligand bridging and are thus closest to the atoms of the following layer. Together with uncoordinated oxygen atoms of the carboxylate groups and the interstitial water molecules they form a complex hydrogen bonding network which is not discussed here in detail (Table 2).

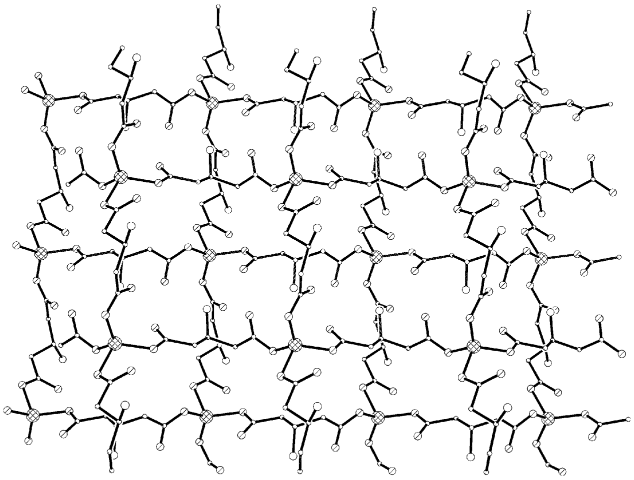

Fig. 3 Projection onto a bilayer in Zn(β-GluH)$_2$(H$_2$O)$_3$. Zn-atoms of a given layer are above the centre of the rectangle spanned by four Zn-atoms of the neighbouring layer.

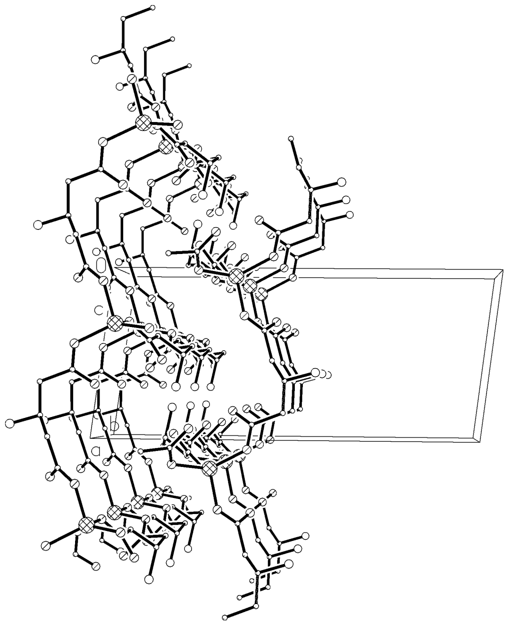

Fig. 4 View parallel to the bilayer shown in Fig. 3, demonstrating the indentation of the layers. Water molecules are omitted for clarity.

The quasi-square pores in each layer are equivalent by symmetry and determined by the size of the 32-membered rings. With an area of the rectangles of 80.59 Å^2, the sheets represent undulated wide-mesh nets as illustrated in Figs 2–4. Because in the stacking the nets are not placed exactly on top of each other, but rather shifted such that each mesh is centered by the corner atom of the neighbouring net(s), no straight and wide channels are formed in the crystal.

Lithium hydrogen-β-glutamate hydrate. Crystals of [Li-(β-GluH)(H$_2$O)] are monoclinic, space group $P2_1/c$, with Z = 4 formula units in the unit cell. The asymmetric unit contains one lithium cation, one hydrogen-β-glutamate anion (in its *anti*-conformation) and one water molecule (Fig. 5). The components are aggregated to form layers in which each metal cation connects three anions *via* Li–O coordinative bonds. The quasi-tetrahedral coordination sphere is completed by the water molecule. Conversely, each anion is connected to three cations

Table 2 Hydrogen bond lengths [Å] and angles [°]. For atomic numbering see Fig. 1 and 5

$Zn(\beta\text{-}GluH)_2(H_2O)_3$				
D–H ··· A	*d*(D–H)	*d*(H ··· A)	*d*(D ··· A)	<(DHA)
O(3)–H(6)–O(15)^{a}	0.84(4)	2.08(4)	2.885(2)	159(3)
O(3)–H(5)–O(14)^{b}	0.83(3)	1.95(3)	2.771(2)	172(3)
O(2)–H(4)–O(17)^{c}	0.86(3)	2.04(3)	2.837(2)	153(3)
O(2)–H(3)–O(12)^{d}	0.84(4)	2.00(4)	2.833(2)	172(3)
O(1)–H(2)–O(2)^{c}	0.88(4)	1.92(4)	2.779(3)	165(3)
O(1)–H(1)–O(11)^{d}	0.91(5)	2.11(5)	2.932(3)	149(4)
N(2)–H(04)–O(11)^{e}	0.91(4)	1.98(4)	2.876(3)	168(3)
N(1)–H(03)–O(1)^{f}	0.94(3)	2.34(3)	3.139(3)	143(2)
N(1)–H(02)–O(3)	0.90(3)	1.82(3)	2.720(2)	178(3)
N(1)–H(01)–O(16)^{g}	0.90(3)	2.21(3)	3.055(2)	155(2)
$Li(\beta\text{-}GluH)(H_2O)$				
O(01)–H(02)–O(1)^{h}	0.86(2)	1.93(2)	2.782(1)	172(2)
O(01)–H(01)–O(2)^{i}	0.92(2)	1.86(2)	2.774(1)	176(2)
N(1)–H(3)–O(01)	0.91(2)	2.35(2)	3.148(1)	146(1)
N(1)–H(2)–O(1)^{i}	0.91(2)	1.99(2)	2.844(1)	155(2)
N(1)–H(1)–O(4)^{k}	0.95(2)	1.84(2)	2.789(2)	177(2)

Symmetry transformations used to generate equivalent atoms: a $x - 1/2, -y + 1/2, z - 1/2$. b $-x, -y, -z$. c $-x + 1, -y + 1, -z$. d $x + 1, y, z$. e $-x + 1/2, y + 1/2, -z + 1/2$. f $-x + 1, -y + 1, -z$. g $-x, -y + 1, -z$. h $x - 1, y, z$. i $-x, -y + 2, -z$. k $x, -y + 3/2, z - 1/2$.

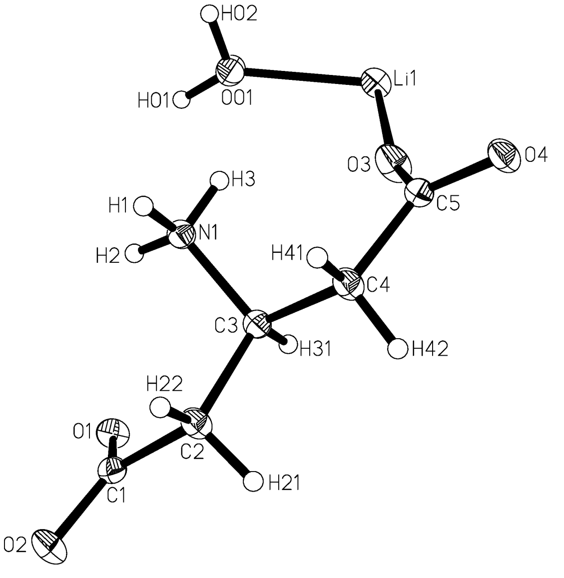

Fig. 5 Asymmetric unit in the structure of $Li(\beta\text{-}GluH)(H_2O)$ with atomic numbering (ORTEP drawing with 50% probability ellipsoids). Selected bond lengths [Å], angles [°] and symmetry transformations: Li(1)–O(2)^2 1.946(2), Li(1)–O(3) 1.890(2), Li(1)–O(4)^1 1.940(2), Li(1)–O(01) 1.987(2); O(3)–Li(1)–O(4)^1 122.0(1), O(3)–Li(1)–O(2)^2 110.0(1), O(4)^1–Li(1)–O(2)^2 101.1(1), O(3)–Li(1)–O(01) 101.3(1), O(4)^1–Li(1)–O(01) 109.1(1), O(2)^2–Li(1)–O(01) 113.74(10); 1 $-x - 1, -y + 2, -z + 1$; 2 $-x, y + 1/2, -z + 1/2$.

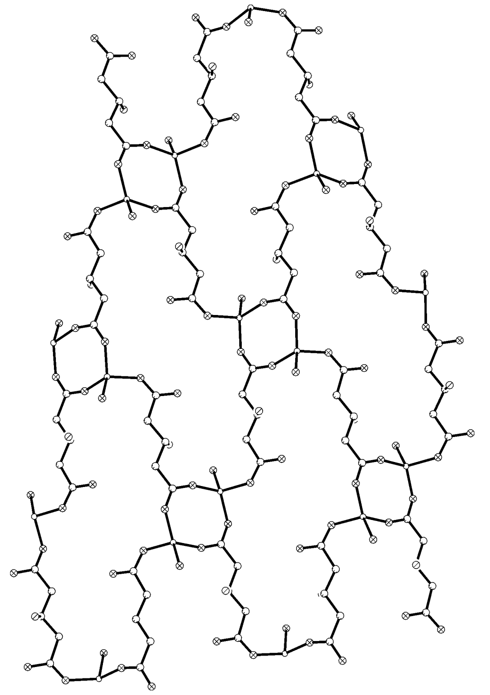

Fig. 6 Projection onto a single layer in the crystalline phase of $Li(\beta\text{-}GluH)(H_2O)$.

through three of its four carboxylate oxygen atoms. One of the two carboxylate groups is therefore bonded terminally to one metal atom, while the other is bridging two metal atoms. All lithium atoms are shared by 8-membered and 32-membered rings. These rings constitute a mixed-mesh network as shown in Fig. 6.

The four lithium atoms of a given 32-membered ring form a parallelogram with Li–Li distances of 8.9554 and 9.546 Å and Li–Li–Li angles of 51.1/128.9°, respectively. The lithium atoms of a given layer are not coplanar, because the plane of the metal atoms of a 32-membered ring is tilted symmetrically against the Li–Li axes of the four 8-membered rings fused to it.

The three Li–O(carboxylate) distances are found in the range 1.890(2)–1.946(2) Å, not very different from the distance Li–O(water) of 1.987(2) Å. The six O–Li–O angles cover the broad range 101.1(1)–122.0(1)°, quite far from the tetrahedral standard. These dimensions are similar to those found *e.g.* for lithium hydrogen bis(L-pyroglutamate) and lithium hydrogen-L-aspartate.[15,19]

As illustrated in two projections parallel to chains of lithium atoms in a layer of this structure (Figs 7 and 8), the sheets are less corrugated than in the zinc compound described above. The eight-membered rings are tilted against the reference plane of the layer and form small channels. Owing to the less pronounced undulation of the layers, the sheets become less indented upon stacking. Neighbouring layers are shifted against each other such that the large rings do not form large channels perpendicular to the layers (Fig. 9). The stacking order is probably largely determined by hydrogen bonding between the layers in which the ammonio group, the water molecule and the carboxylate oxygen atoms are involved. As for the zinc compound (above), details of this network are not discussed further and have been summarized in Table 2.

Discussion

In the present work, the hydrogen-β-glutamate anion [β-GluH]$^-$ was found to be a novel bridging unit for the construction of two-dimensional coordination networks. Depending on

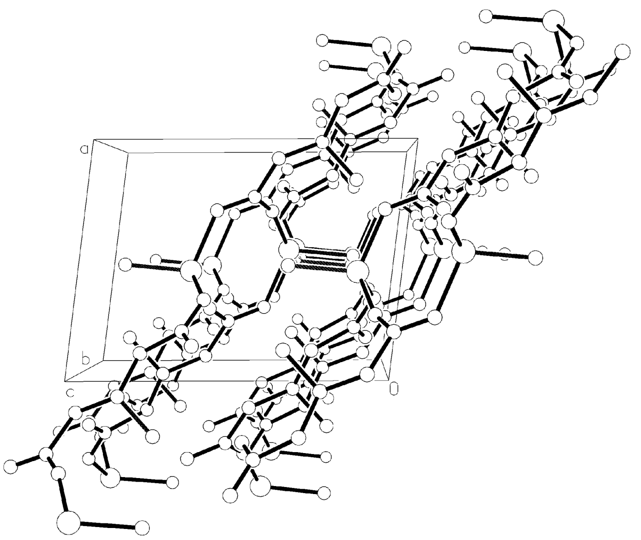

Fig. 7 View parallel to two neighbouring layers in Li(β-GluH)(H_2O).

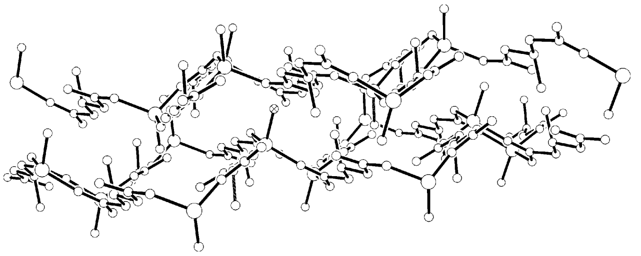

Fig. 8 View parallel to two neighbouring layers in Li(β-GluH)(H_2O), vertical to the projection shown in Fig. 7.

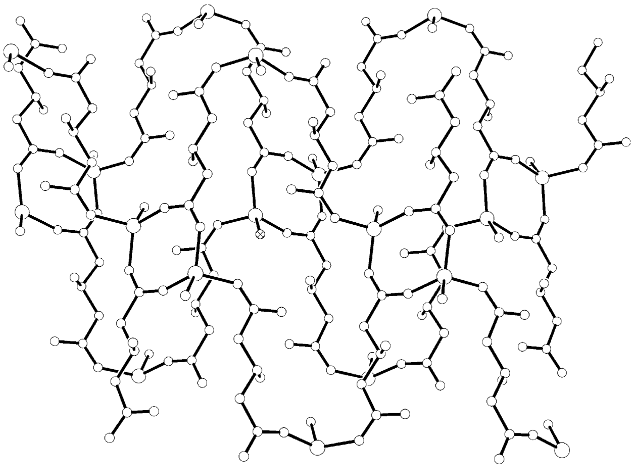

Fig. 9 Projection onto two neighbouring layers in Li(β-GluH)(H_2O).

the nature of the metal and its solvation by residual water molecules, different structural patterns are obtained, for which 32-membered rings are a common motif. This ring appears as a uniform mesh in the sheets of the zinc complex, where the zinc atoms form an almost square grid (Fig. 2), while the same ring appears as an elongated mesh based on a parallelogram of lithium atoms in the mixed-mesh network of the lithium complex, complemented by 8-membered rings which in total share eight edges of a given large ring (Fig. 6).

The coordination of zinc and lithium by hydrogen-β-glutamate is entirely different from the modes observed for metal hydrogen-α-glutamates, where the anions are found to be predominantly chelating.[3] No doubt this difference originates largely from the variation in chelate ring size.

Though based on a dicarboxylic acid, the $[\beta\text{-GluH}]^-$ anion has a reduced negative charge owing to the positively charged ammonio group in the center of the carbon chain connecting the carboxylate groups (Scheme 1). Consequently, the stoichiometry of its metal(II) salts (1 : 2) differs from that of analogous *glutarates* (1 : 1).

In very recent literature the crystal structure of a cobalt(+2) glutarate(−2) [Co(Glut)] has been presented.[20] This compound was shown to have a *three*-dimensional structure based on rectangular-grid layers of tetra-coordinated cobalt atoms connected solely by carboxylate groups. These faces are attached to the alkylidene chains into a pillared structure, with the $(CH_2)_3$ chains in both their *gauche*- and *anti*-conformation. The mesh of the rectangular-grid is based on a 16-membered ring with Co–Co distances of 4.64 and 4.81 Å.

The different structures of metal *glutarates* and metal *hydrogen-β-glutamates* are just two examples which indicate the scope for the construction of complementary complex frameworks with these two ligands.

Acknowledgements

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