Zinc (Hydrogen-β-glutamate)-chloride Hydrate [Zn (β-GluH)Cl(H_2O)], a One-dimensional Coordination Polymer

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Z. Naturforsch. **58b,** 395 – 398 (2003); received January 24, 2003

Zinc (hydrogen-β-glutamate) chloride hydrate is readily prepared from equimolar quantities of [Zn (β-GluH)$_2$] and $ZnCl_2$ in water. The crystal structure shows a coordination polymer with zinc atoms bridged by the 3-ammonio-glutarate ligand. The tetrahedral coordination sphere of the metal atom is completed by the chloride anion and the water molecule.

Key words: Zinc Complex, β-Glutamate Complex, Coordination Polymer, Bioinorganic Chemistry

Introduction

Aspartes and α-glutamates of the alkali (Li, Na, K) and alkaline earth metals (Mg, Ca) are important components for many preparations in the pharmaceutical industry [1]. L-aspartic and L-α-glutamic acid in particular, which are ubiquitous in nature, have been shown to form a large variety of salts and complexes with these metals both in aqueous solution and in the solid state depending on the pH of the system. This coordination chemistry is of prime importance for many areas of Bioinorganic Chemistry in general, and for biomineralization in particular, and this relevance is responsible for the therapeutic and diagnostic value of the compounds.

In their complexes, aspartic or α-glutamic acid may appear as mono- or dianions [L-AspH]$^-$, [L-Asp]$^{2-}$, [L-α-GluH]$^-$, and [L-α-Glu]$^{2-}$, functioning as counterions or as potentially multidentate donor ligands. Particularly advantageous therapeutical effects have been demonstrated for formulations where the aspartate or glutamate anions are combined with other anions such as chloride, as in [Mg(L-AspH)]Cl(H_2O)$_3$ [2]. Trace metals like zinc have also been included into recent investigations and the stoichiometry and structures of several α-aspartates and -glutamates are documented [3 – 5]. Apart from standard binary compounds, a mixed-ligand complex [Zn(L-AspH)Cl] was obtained and shown to be a two-dimensional coordination polymer [6].

The coordination chemistry of β-amino acids, which are rare in nature, is much less developed and it was only very recently that β-glutamates have been used as ligands for Main Group and Transition Metals [7]. Following work on a "binary" zinc β-glutamate [Zn (β-GluH)$_2$] [8], we now report on the preparation and crystal structure of the title compound.

Results

Zinc hydrogen-β-glutamate chloride was prepared by the reaction of zinc bis(hydrogen-β-glutamate) monohydrate [8] with an equimolar quantity of zinc dichloride in water. After a short reflux period the reaction mixture was set aside to allow for crystallization. After several months large crystals of the monohydrate had formed in 56% yield. Owing to the gradual loss of water the product has no well-defined melting point. The IR spectrum (in KBr) shows all bands expected for the hydrogen-β-glutamate ligand as already observed for [Zn (β-GluH)$_2$]. The elemental analysis data are in agreement with calculated values.

$$\mathrm{Zn}\,(\beta\text{-GluH})_2(\mathrm{H_2O}) + \mathrm{ZnCl_2} + \mathrm{H_2O} \xrightarrow[\mathrm{H_2O}]{} 2\ \mathrm{Zn}\,(\beta\text{-GluH})\mathrm{Cl}(\mathrm{H_2O})$$

Crystals of [Zn (β-GluH)Cl(H_2O)] are monoclinic, space group $P2_1/c$, with $Z = 4$ formula units in the cell. The asymmetric unit comprises one zinc and one chlorine atom, one hydrogen-β-glutamate anion with a protonated amino group and one water molecule (Fig. 1).

Each hydrogen-β-glutamate ligand is in a bridging position between two zinc atoms employing its

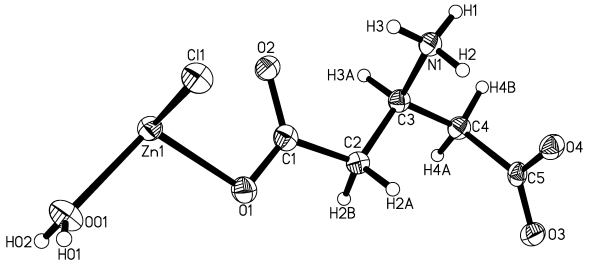

Fig. 1. Asymmetric unit in the crystalline phase of [Zn (β-GluH)Cl(H_2O)] with atomic numbering (ORTEP drawing [9c] with 50% probability ellipsoids).

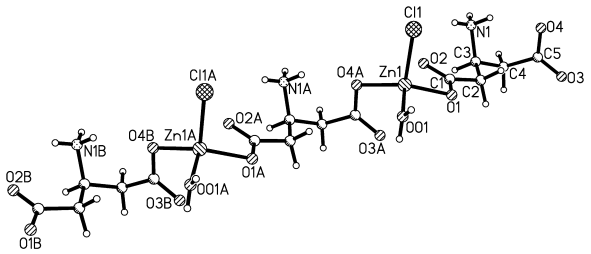

Fig. 2. Coordination sphere of the zinc dications in [Zn (β-GluH)Cl(H_2O)], illustrating the formation of chains. Selected bond lenghts [Å], angles [°] and symmetry transformation: Zn1-O1 2.009(2), Zn1-O01 1.997(2), Zn1-Cl1 2.274(1), Zn1-O4A^a 2.003(2); O1-Zn1-O01 104.78(10), O1-Zn1-Cl1 102.54(7), O1-Zn1-O4A^a 130.70(9), O01-Zn1-Cl1 101.14(8), O01-Zn1-O4A^a 106.76(10), Cl1-Zn1-O4A^a 107.31(6); ^{a} $x, y, z-1$.

oxygen atoms O1 and O4 of different carboxylate groups as donor atoms. With the chlorine atom and the water molecule as additional donors, the zinc atoms are quasi-tetrahedrally coordinated (Fig. 2). With the exception of the angle O1-Zn1-O4A [130.70(9)°] all angles at the zinc atom are close to the tetrahedral standard [101.14(8) – 107.31(6)°]. This distortion may be due to weak donor-acceptor interactions Zn1-O2 and Zn1-O3A at distances of 2.591 and 2.538 Å. These distances are to be compared with the three distances Zn1-O1, Zn1-O4A and Zn1-O01 to the three nearest oxygen neighbours [2.009(2), 2.003(2) and 1.997(2) Å, respectively], which are much shorter. The Zn1-Cl1 distance is found at 2.2741(8) Å, in fair agreement with the value published for [Zn (L-AspH)Cl], 2.225(1) Å.

The C1-C4 part of the carbon chain in the β-GluH$^-$ ligand is coplanar with a dihedral angle C1-C2-C3-C4 of $-172.9(2)°$, representing a *trans* conformation. The atoms of the carboxylate group C1(O1/O2) are also in this plane with dihedral angles O1-C1-C2-C3 and O2-C1-C2-C3 at $-179.9(3)$ and 0.6(4)°, respectively. By contrast, the carbon atom C5 is off this plane [with a dihedral angle C5-C4-C3-C2 at $-56.6(3)°$] owing to a gauche conformation of this part of the skeleton. It should be noted that in [Zn (β-GluH)$_2$](H_2O)$_3$ the anions are fully extended in an all-*trans* conformation [8]. Through the *trans-gauche* conformation of the [β-GluH]$^-$ anion the maximum possible (mirror) symmetry is violated and the ligand is chiral.

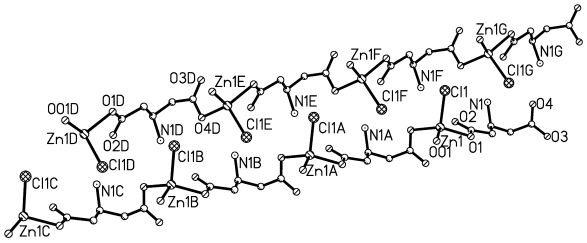

Fig. 3. Pairwise aggregation of chains in the crystalline phase of [Zn (β-GluH)Cl(H_2O)].

The connectivity and configurational / conformational pattern leads to a one-dimensional coordination polymer, as illustrated in Fig. 3. Pairs of chains run parallel to the crystallographic *c*-axis, with shortest contacts between the chlorine atoms of one chain and the ammonio functions of the neighbouring chain. Details of the packing of the chains are therefore largely determined by electrostatic forces and by hydrogen bonds.

This is also true for the details of the internal geometry of the chains where interactions of the water molecule, the ammonio function and the two carboxylate groups are most prominent. Particularly short and almost linear O-H–O bonding is found between O2D and O3E as the acceptor atoms and the water molecule as the donor (Table 1, Fig. 4). Further short contacts exist between O2 and O4 on one hand and N1-H2 and N1-H3 on the other. A few longer and more strongly bent hydrogen bridges have also been included in Table 1 (but are not drawn in Fig. 4), their contribution however is probably much less significant.

In a given chain all the [β-GluH]$^-$ anions have the same configuration, but in the neighbouring chain this configuration is inverted. The crystal is thus a packing of racemic chain components.

Conclusions

The present study is an extension of preparative work which had led to the isolation and structural characterization of the first zinc β-glutamate, the "binary compound" [Zn (β-GluH)$_2$](H_2O)$_3$. This com-

Table 1. Hydrogen bonding in [Zn (β-GluH)Cl(H_2O)]. For atomic numbering, see Fig. 4.

D-H-A	d(D-H) [Å]	d(H···A) [Å]	D-H···A [°]	d(D···A) [Å]
N1-H1-Cl1A[a]	0.87(5)	2.40(5)	163(4)	3.242(3)
N1-H2-Cl1B[b]	0.91(4)	2.74(4)	137(3)	3.468(3)
N1-H2-O2B[b]	0.91(4)	2.53(4)	113(3)	3.000(3)
N1-H2-O4	0.91(4)	2.19(4)	123(3)	2.803(3)
N1-H3-O4C[c]	0.83(4)	2.54(4)	136(3)	3.193(4)
N1-H3-O2	0.83(4)	2.30(4)	129(3)	2.898(4)
O01-H01-O2D[d]	0.81(6)	1.99(6)	160(5)	2.771(3)
O01-H02-O3E[e]	0.83(5)	1.80(5)	179(5)	2.638(3)

Symmetry transformations used to generate equivalent atoms: [a] $x-1, -y+1/2, z+1/2$; [b] $x, -y+1/2, z+1/2$; [c] $x, -y+1/2, z-1/2$; [d] $x+1, y, z$; [e] $-x, -y+1, -z+1$.

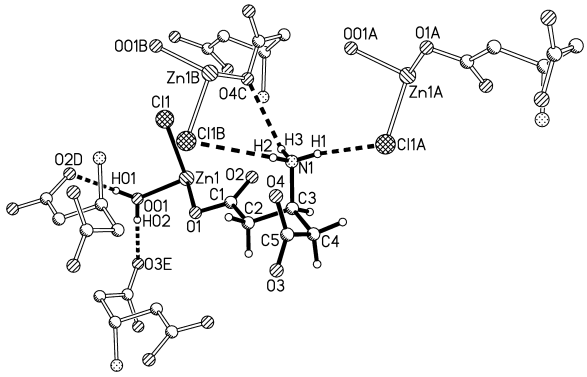

Fig. 4. Hydrogen bonding in crystalline [Zn (β-GluH)Cl(H_2O)]. The asymmetric unit is indicated by filled lines, units generated by symmetry transformations are marked with blank lines. Only the most prominent hydrogen bonds are indicated in this figure; for a complete list and all bond lengths, angles and symmetry transformations, see Table 1.

plex has a layer structure with a square grid of zinc atoms spanned by fully and symmetrically extended β-GluH$^-$ bridging units [8].

It has now been shown that β-glutamic acid can also be employed for the synthesis of a mixed-anion zinc complex of the formula [Zn (β-GluH)Cl(H_2O)]. Although both results may be taken as simply analogous to the chemistry of α-aspartic and α-glutamic acid [1–7], the structural details of the products are noteworthy. In the new compound the dimensionality of the array is reduced to a chain structure with the zinc atoms bridged by conformationally unsymmetrical (*trans-gauche*) β-GluH$^-$ units.

It is particularly interesting that in [Zn (β-GluH)Cl(H_2O)] the chloride anion is part of the innermost coordination sphere of the zinc dication and thus obviously competes favourably not only with other donor centers still available in the hydrogen-β-glutamate anion, but also with water molecules. This high Zn-Cl affinity has already been observed in [Zn (L-AspH)Cl] [6] and therefore should not be taken only as an exception arising from *e. g.* packing effects. Although interacting with a chloride anion, the zinc atom is observed to remain only four-coordinated in a distorted tetrahedral geometry. In most other "binary" zinc aspartates or glutamates the coordination number rises to five or even six [1–7].

Experimental Section

Zinc hydrogen-β-glutamate chloride hydrate, [zinc (3-ammonio-glutarate) chloride hydrate, zinc (3-ammonio-pentane-1,5-dioate) chloride hydrate], Zn (β-GluH)Cl(H_2O).

[Zn (β-GluH)$_2$]H_2O (70 mg, 0.19 mmol) (obtained *via* a synthesis recently published [8]) is suspended in a solution of anhydrous $ZnCl_2$ (25.3 mg, 0.19 mmol) in 10 ml of bidistilled water and the mixture is stirred for 4 h at 20 °C. Subsequently the solution is heated to reflux temperature for 15 min and allowed to cool to 20 °C. For crystal growth the volume of the solution is reduced to 5 ml in a vacuum and the flask is set aside for 8 months at room temperature. Colourless crystals separate in 56% yield (55 mg).

Elemental analysis calcd. for Zn (β-GluH)Cl(H_2O)

($C_5H_{11}Cl_1N_1O_5Zn_1$): C 22.67, H 3.80, N 5.31, O 30.19, Cl 13.38 Zn 24.68; found C 22.58, H 3.84, N 5.26, O 30.10, Cl 13.77, Zn 24.50%.

IR (KBr, cm^{-1}): 3350–2900, s, br, $\nu(NH_3^+)$, ν(C-H), ν(O-H); 1607, s, br, $\delta_{asym}(NH_3^+)$, $\delta_{sym}(NH_3^+)$, ν_{asym}(C-O); 1409, s, br, ν_{sym}(C-O), δ(C-H); 1000, m, ν(C-N).

Structure determination

The crystalline sample was placed in 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$_\alpha$ (λ = 0.71073 Å) radiation at −130 °C. The structure was solved by direct methods using SHELXS-97 [9a] and refined by full-matrix least-squares calculations on F^2 with SHELXL-97 [9b]. Non-H-atoms were refined with anisotropic thermal parameters. C-H atoms were placed in idealized positions and refined using a riding model with fixed isotropic contributions, whereas the N-H and O-H atoms were located and refined with isotropic contributions. An extinction correction was applied using DELABS, maximum and minimum transmission 0.895 and 0.642.

Crystal data for $C_5H_{10}ClNO_5Zn$

M = 264.96, monoclinic, $a = 6.1151(2)$, $b = 17.8393(7)$, $c = 8.2369(2)$ Å, $\beta = 107.618(3)^\circ$, space group $P2_1/c$, $Z = 4$, $V = 859.22(5)$ Å^3, μ(Mo-K$_\alpha$) = 3.16 mm^{-1}, 13841 measured and 1884 unique reflections [$R_{\text{int}} = 0.0788$], $wR2 = 0.0687$, $R = 0.0334$ [$I \geq 2\sigma(I)$] and 138 parameters. The function minimized was $wR2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.02930$, $b = 0.45$. Residual electron density 0.440/−0.398 eÅ^{-3}.

Displacement parameters and complete tables of interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1 EZ, UK. The data are available on request on quoting CCDS- 201841.

Acknowledgement

This work was supported by Fonds der Chemischen Industrie.

[1] H. Schmidbaur, H. G. Classen, J. Helbig, Angew. Chem. Int. Ed. **29**, 1090 (1990).
[2] H. Schmidbaur, D. L. Wilkinson, A. Schier, J. Helbig, G. Manninger, New J. Chem. **18**, 507 (1994).
[3] T. Doyne, R. Pepinsky, T. Watanabe, Acta Crystallogr. **10**, 438 (1957).
[4] C. Grammaccioli, Acta Crystallogr. **21**, 600 (1988).
[5] H. Schmidbaur, I. Bach, D. L. Wilkinson, G. Müller, Chem. Ber. **121**, 1441 (1988).
[6] H. Schmidbaur, I. Bach, J. Riede, G. Müller, J. Helbig, G. Hopf, Chem. Ber. **120**, 867 (1987).
[7] a) F. Wiesbrock, S. Nogai, A. Schier, H. Schmidbaur, Helv. Chim. Acta **85**, 1151 (2002), and references therein; b) F. Wiesbrock, A. Schier, H. Schmidbaur, Z. Naturforsch. **57b**, 251 (2002); c) F. Wiesbrock, H. Schmidbaur, J. Chem. Soc., Dalton Trans. 4703 (2002).
[8] F. Wiesbrock, H. Schmidbaur, J. Chem. Soc., Dalton Trans. 3201 (2002) and references therein.
[9] a) G. M. Sheldrick, SHELXS-97, Program for structure solution, University of Göttingen (1997); b) G. M. Sheldrick, SHELXL-97, Program for structure analysis, University of Göttingen (1997); c) C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN (1976).