Scientific paper

# Syntheses, Crystal Structures and Thermal Behaviour of Novel L-Alanine Halogenide Compounds

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*Received: 02-04-2008*

***Dedicated to the memory of Professor Ljubo Golič***

## Abstract

Two new L-alanine compounds (alanine alaninium triiodide (1), s.g. $P2_12_12_1$, a = 8.366(2) Å, b = 8.912(2) Å, c = 41.889(8) Å and alanine $SrCl_2$ $3H_2O$ (2), s.g. $P2_1$, a = 8.540(2) Å, b = 7.167(1) Å, c = 8.769(2) Å, β = 95.02(3)°) have been prepared and characterised by X-ray single crystal analysis. The crystal structure of (1) features the presence of two independent molecules of alanine, alaninium and triiodide, respectively, in the asymmetric unit, with a very strong hydrogen bond between the carboxylate groups of alanine and alaninium. Compound (2) is composed of infinite zig-zag chains of $[SrO_7Cl]$-polyhedra, with alanine molecules and chloride ions in the interstices. By the study of the thermal behaviour of (1) via thermogravimetry and temperature resolved X-ray powder diffraction it was found that the compound is stable up to approx. 363 K and that the thermal expansion along *c* is only about 1/3 compared to *a* and *b*.

**Keywords:** Alanine, crystal structure, amino-acid, coordination compounds, thermal properties

## 1. Introduction

The chemical flexibility of amino acids is the main reason for the large variety of compounds resulting from reactions of amino acids with inorganic salts, acids or hydroxides. In the past, we have systematically investigated such compounds of glycine[1,2 (and references therein)]. Here the neutral glycine molecule as a constituent of crystal structures with inorganic salts usually adapts the *zwitterionic* form, with the dissociated carboxyl group and protonated amino group. However, glycine can also act as cationic (glycinium) or anionic (glycinate) constituent in corresponding systems. In addition, degrees of conformational flexibility concerning a rotation of the carboxyl group around the C–C-bond increase the variety of crystal structures in this large family of compounds.

We have now focused on compounds of L-alanine as the smallest possible chiral amino acid, $CH_3NH_2CHCOOH$ or its *zwitterionic* form, $CH_3(NH_3)^+CH(COO)^-$ (Fig. 1).

The chirality of L-alanine enforces non-centrosymmetry of crystal structures of its compounds. This is an important aspect in addition to the above mentioned chemical and conformational flexibility (both of which are valid for alanine as well) for the search for new non-centrosymmetrical materials with certain desired physical properties, such as in the field of non-linear optics.[3] Considering the chemistry, a very large number of inorganic alanine, alaninium or alaninate compounds (further abbreviated as *alaH* for $CH_3NH_2CHCOOH$, *alaH*$_2$ for $CH_3(NH_3)^+CHCOOH$ and *ala* for $CH_3NH_2CHCOO^-$, respectively) is conceivable. A search through the crystallographic data banks (CSD[4], PC–PDF[5]) revealed over 280 alanine compounds. However, in most of these substances alanine is combined with other organic molecules. Only 33 compounds of *ala*H, *ala*$H_2$ or *ala* with inorganic materials, including racemates, were found,. As expected, most of the DL-alanine compounds are centrosymmetric, only one of them is non-centrosymmetrical: DL-*ala*H $CdCl_2$[6], as well as DL-alanine[7] itself. In this work, we present the crystal structures of two new alanine halogenide species,

L-alanine alaninium triiodide, (*ala*H)(*ala*$H_2$)$I_3$ (1), s.g. $P2_12_12_1$ and L-alanine $SrCl_2 \cdot 3H_2O$, (*ala*H) $SrCl_2 \cdot 3H_2O$ (2), s.g. $P2_1$.

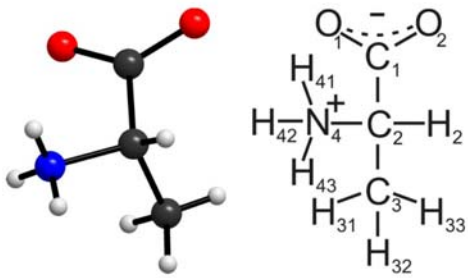


**Figure 1.** Alanine as the smallest chiral amino acid in its *zwitterionic* form (left), numbering scheme used throughout this work. In (1), atoms from different moieties are labelled a,b,c,d.

# 2. Experimental

## 2. 1. Syntheses

The crystals of (*ala*H)(*ala*$H_2$)$I_3$ (1) were obtained at room temperature by slow evaporation of an aqueous solutions of L-alanine with a surplus of dilute hydroiodic acid. A partial decomposition of the hydroiodic acid during the crystallisation period of several weeks yielded the triiodide anions as constituents of (1). (*ala*H) $SrCl_2 \cdot 3H_2O$ (2) crystallised at room temperature from an aqueous solution of L-alanine and $SrCl_2$ $2H_2O$ with stoichiometric mixture of the constituents (1:1) in colourless crystals in size of up to a few millimeters.

## 2. 2. Structure Determination and Refinement

Single-crystal X-ray intensity data of the title compounds were collected at 293 K on a Nonius Kappa diffractometer with CCD area detector, using Mo $K\alpha$-radiation ($\lambda$ = 0.71073 Å).

The intensity data were processed with the Nonius programme suite DENZO-SMN[7] and corrected for Lorentz, polarisation, background and absorption effects.[9] The crystal structures were determined by automatic Patterson method and subsequent Fourier and difference Fourier syntheses, followed by full-matrix least-squares refinements on $F^2$.[10] In (2), the hydrogen atoms could be located from the difference Fourier map. In the case of (1), the location of the hydrogen atoms was not straightforward (because of the presence of heavy iodine atoms). However, each of the linear triiodide anions $I_3^-$ needs a positive alaninium group in the structure. Non-H atoms were treated anisotropically, H atoms isotropically and unrestrained. The refinements converged at *R*-values of 0.019 and 0.028.

Crystal data, details of the measurements and the refinements are given in Table 1. Further details of the crys-

**Table 1.** Crystal data and details of the intensity measurements and structure refinements for compounds (1) and (2).

| | **(1) (*ala*H)(*ala*$H_2$)$I_3$** | **(2) (*ala*H)·$SrCl_2$·$3H_2O$** |
|---|---|---|
| Formula | $C_6H_{15}I_3N_2O_4$ | $C_3H_{13}Cl_2NO_5Sr$ |
| $M_r$ | 559.90 | 301.66 |
| Habitus, colour | Prism, purple | Prism, colourless |
| Crystal size, $mm^3$ | 0.2 × 0.2 × 0.1 | 0.14 × 0.08 × 0.08 |
| Crystal system | Orthorhombic | Monoclinic |
| Space group | $P2_12_12_1$ | $P2_1$ |
| *a*, Å | 8.366(2) | 8.540(2) |
| *b*, Å | 8.912(2) | 7.1670(10) |
| *c*, Å | 41.889(2) | 8.769(2) |
| $\beta$, deg | – | 95.02(3) |
| *V*, $Å^3$ | 3123.2(12) | 534.7(2) |
| Z | 8 | 2 |
| Temperature, K | 293 | 293 |
| $D_{calc}$, g $cm^{-3}$ | 2.382 | 1.874 |
| $\mu$(Mo$K_\alpha$), $cm^{-1}$ | 6.004 | 5.529 |
| *F*(000), e | 2048 | 300 |
| *hkl* range | ±11, ±12, ±59 | –11/12, –8/10, ±12 |
| Refl. Measured | 28863 | 2687 |
| Refl. Unique | 9442 | 2628 |
| $R_{int}$ | 0.0287 | 0.000 |
| Refined Parameters | 393 | 162 |
| *R*(F) (for *F*o>4σ($F_o$)) | 0.0276 | 0.0190 |
| w*R*($F^2$) (all reflections) | 0.0528 | 0.0491 |
| Flack parameter[11] | –0.009(18) | 0.008(5) |
| GooF ($F^2$) | 1.019 | 1.038 |
| Residue max / min, e $Å^{-3}$ | 0.69 / –0.77 | 0.44 / –0.59 |

**Table 2.** Selected intramolecular distances [Å], angles and torsion angles [°] of the alanine moities for compounds (1) and (2). Different moieties within (1) are labelled a, b, c, and d.

| Distances | C1–O1 | C1–O2 | C1–C2 | C2–C3 | C2–N4 |
|---|---|---|---|---|---|
| (1)a | 1.270(4) | 1.221(4) | 1.518(4) | 1.508(7) | 1.484(4) |
| (1)b | 1.280(4) | 1.224(4) | 1.512(5) | 1.513(6) | 1.489(5) |
| (1)c | 1.275(4) | 1.229(4) | 1.518(4) | 1.522(5) | 1.494(4) |
| (1)d | 1.279(4) | 1.219(4) | 1.522(5) | 1.503(6) | 1.488(5) |
| (2) | 1.253(3) | 1.257(3) | 1.522(2) | 1.523(3) | 1.486(3) |

| Angles | O1–C1–O2 | C1–C2–C3 | C1–C2–N4 | C3–C2–N4 | O2–C1–C2–N4 |
|---|---|---|---|---|---|
| (1)a | 126.6(3) | 112.6(4) | 109.3(3) | 109.9(3) | –171.4(3) |
| (1)b | 125.9(3) | 109.9(3) | 107.9(3) | 109.9(3) | –166.0(3) |
| (1)c | 126.7(3) | 110.4(3) | 108.7(3) | 110.6(3) | 166.1(3) |
| (1)d | 126.0(3) | 110(2) | 108.0(3) | 110.7(4) | –179.0(3) |
| (2) | 124.1(2) | 109.2(2) | 110.1(2) | 109.9(2) | 156.7(2) |

**Table 3.** Sr–O-distances [Å] and calculated bond-valence sums of the cations for compound (2).

| Compound (2) | | |
|---|---|---|
| Sr-O1w | 2.521(2) | 0.336 |
| Sr-O1 | 2.593(2) | 0.277 |
| Sr-O2w | 2.602(2) | 0.270 |
| Sr-O2 | 2.604(2) | 0.269 |
| Sr-O2 | 2.613(2) | 0.262 |
| Sr-O3w | 2.686(2) | 0.215 |
| Sr-O1 | 2.849(2) | 0.139 |
| Sr-Cl | 12.8910(9) | 0.334 |
| | mean 2.67 | 2.10 v.u. |

**Table 4.** Hydrogen bonds in compounds (1) and (2).

| D–H···A | d(D–H) | d(H···A) | d(D···A) | <DHA |
|---|---|---|---|---|
| **Compound (1)** | | | | |
| O1a–H1a···O1d | 1.06(7) | 1.41(7) | 2.475(3) | 177(7) |
| N4a–H41a···O2c | 0.93(4) | 1.87(4) | 2.742(4) | 155(3) |
| N4a–H42a···O1b | 0.94(5) | 2.29(5) | 2.924(4) | 124(3) |
| N4a–H43a···I3 | 0.95(4) | 2.76(5) | 3.698(3) | 170(3) |
| O1b–H1b···O1c | 1.00(2) | 1.51(2) | 2.505(3) | 178(7) |
| N4b–H41b···I4 | 0.87(4) | 3.04(4) | 3.858(4) | 159(3) |
| N4b–H42b···O1a | 0.77(5) | 2.30(5) | 2.919(4) | 139(5) |
| N4b–H43b···O2d | 0.97(5) | 1.84(5) | 2.764(4) | 158(5) |
| N4c–H41c···O1c | 0.89(4) | 2.06(4) | 2.844(4) | 147(4) |
| N4c–H42c···I1 | 0.92(5) | 2.94(4) | 3.711(3) | 142(3) |
| N4c–H43c···O2b | 0.87(4) | 1.96(5) | 2.801(4) | 162(4) |
| N4d–H41d···I6 | 0.85(4) | 2.91(4) | 3.731(4) | 162(3) |
| N4d–H42d···I6 | 0.72(8) | 3.08(8) | 3.726(4) | 150(7) |
| N4d–H43d···O2a | 0.92(4) | 1.82(4) | 2.728(4) | 166(4) |
| **Compound (2)** | | | | |
| N4–H41···Cl2 | 0.96(5) | 2.48(4) | 3.352(2) | 151(3) |
| N4–H42···Cl1 | 0.84(4) | 2.49(4) | 3.273(2) | 156(4) |
| N4–H43···Cl2 | 0.87(4) | 2.40(4) | 3.257(2) | 168(3) |
| O1w–H1w1···Cl2 | 0.86(5) | 2.33(5) | 3.164(3) | 164(4) |
| O1w–H2w1···O2w | 0.87(7) | 1.90(7) | 2.745(3) | 165(6) |
| O2w–H1w2···Cl2 | 0.88(4) | 2.27(4) | 3.106(2) | 158(5) |
| O2w–H2w2···O3w | 0.76(4) | 2.04(5) | 2.770(3) | 162(4) |
| O3w–H1w3···Cl2 | 0.84(4) | 2.32(4) | 3.151(2) | 171(4) |
| O3w–H2w3···Cl1 | 0.87(5) | 2.29(5) | 3.133(2) | 165(4) |

tals structures are available from the Cambridge Crystallographic Data Centre[12] with quotation numbers CCDC 675839 for (1) and CCDC 675838 for (2). Selected interatomic distances and angles as well as calculated bond valence sums for the Sr cation in (2) are given in Tables 2 and 3, hydrogen bonding is listed in Table 4. Observed and calculated structure factors are available from the authors.

In addition to the single crystal analyses, powder diffraction data were collected and submitted to the Powder Diffraction File[13] for the title compounds (PDF-Numbers: 56-1965 for (1) and 56-1964 for (2)). Although single crystal data are superior as far as determination and refinement of the structural parameters (atomic positions and displacement parameters) are concerned, more accurate lattice parameters were obtained from the powder data by means of the Rietveld method.[14] Powder data were collected at room temperature on a Philips PW3020 X-ray powder diffractometer with Bragg-Brentano geometry.

## 2. 3. Thermal Analyses

Temperature resolved X-ray powder data for (1) were collected on a PHILIPS PW 3050 based X'PERT MPD diffractometer in Debye-Scherrer geometry equipped with an in-house built capillary spinner and a RAYTECH PSD (position sensitive detector). For the monochromatic, parallel-beam X-ray source ($\lambda$ = 1.54056 Å) a ceramic-type copper tube (40 kV, 40 mA) in combination with a PHILIPS hybrid-monochromator was used. A soller slit of 1.15° axial divergence was inserted on the primary side to reduce the peak asymmetry. The goniometer radius of the secondary side was 343.8 mm, which corresponds to an angular resolution of 6 mm/° 2θ and a physical detector resolution of 0.011° 2θ. Measurements were performed at 298(1), 307(5), 321(5), 334(5), 343(5), 353(5), 363(5), 373(5) and 383(5) K in a continuous mode, using a fivefold data collection, each set over the range 5–35° 2θ with a step interval of 0.011° 2θ, a scan time of 4 h, and an angular PSD opening of 4° 2θ. For es-

tablishing the non-ambient conditions a modified specimen heating device of the HUBER 600 Guinier camera system was used. The determination of the cell parameters was done applying Rietveld refinements with the structural parameters of the single-crystal work using the Bruker TOPAS software.[15]

The TA experiment was performed on a Mettler-Toledo TGA/SDTA-851 System using 70 µl $Al_2O_3$ sample crucibles under $N_2$ (5.5) protective gas with 20 ml $min^{-1}$ flow rate, temperature range 298 – 673 K, and 5 K $min^{-1}$ heating rate. Data were evaluated using the Mettler-Toledo STARe software.[16]

## 3. Results and Discussion

### 3. 1. Structure of Alanine Alaninium Triiodide, $(C_3H_7NO_2)$ $(C_3H_8NO_2)$ $I_3$ (1)

When examining crystals of this compound by means of X-ray diffraction, the first thing we noticed is the unusually large unit cell parameter in the *c* direction – by far the largest found in any compound of alanine with inorganic constituents. At first, we suspected some mistake, but careful study of the reflections as well as unsuccessful attempts to assign other unit cells proved the given unit cell to be correct. The crystal itself is composed of alanine and alaninium molecules as well as triiodide groups, two moieties of each in the asymmetric unit. The triiodide groups are linear and aligned more or less along the [001] direction (Fig. 2a). The structural units are connected to each other by means of an intricate hydrogen bond network, extending from the amino groups and the two acid hydrogen atoms. The latter are remarkable insofar as they are part of two very strong hydrogen bonds between opposing carboxylate oxygen atoms (Fig. 2b), although the hydrogen atoms themselves could not be located very precisely (isotropic displacement parameters of about 0.15 $Å^2$ ). We investigated the possibility of symmetric or disordered hydrogen bonds, but wherever we put the hydrogen atoms, the refinements always gave hydrogen locations clearly to one side of the bond (Fig. 2b). This arrangement is similar as in alanine alaninium nitrate, (*ala*H)(*ala*$H_2$)($NO_3$),[17] where one alaninium ion extends a strong hydrogen bond to an alanine molecule. In contrast to the conformation in the nitrate, where the bridging H-atom is *syn* to the donor and *anti* to the acceptor carboxyl group, the H atom is in *syn*-position to both donor and acceptor carboxyl group in the triiodide (the torsion angles O2a–C1a–O1a–H1a and O2d–C1d–O1d –H1 being 5.89° and 1.61°, respectively) (Fig. 2c).

The position of the H atom clearly justifies the name and formula as given above – there are distinctly two alanine and two alaninium molecules in the asymmetric unit. As stated above, the same situation has been reported for the respective nitrate, but for no other alanine compounds, which either contain the *zwitterionic* (e.g., (*ala*H) $MnCl_2 \cdot 2H_2O$[18]), the cationic (e.g., (*ala*$H_2$)$NO_3$ [19] or (*ala*$H_2$)Cl[20]) or the anionic form (e.g., *cis- and trans*-$Cu^{II}$(*ala*)$_2$[21–24]) exclusively*.

* Note that the crystal structure of (*ala*)$_2$ Ni $4H_2O$ is erroneously reported with space group *Cc*.[25] The chirality of L-alanine prevents the occurrence of any mirror or glide plane symmetry. In an earlier publication[26] *C*2, *Cm* or *Cc* were suggested as possible space groups on the base of X-ray powder diffraction data. A reinvestigation is still pending, but from the given alternatives only *C*2 is possible.

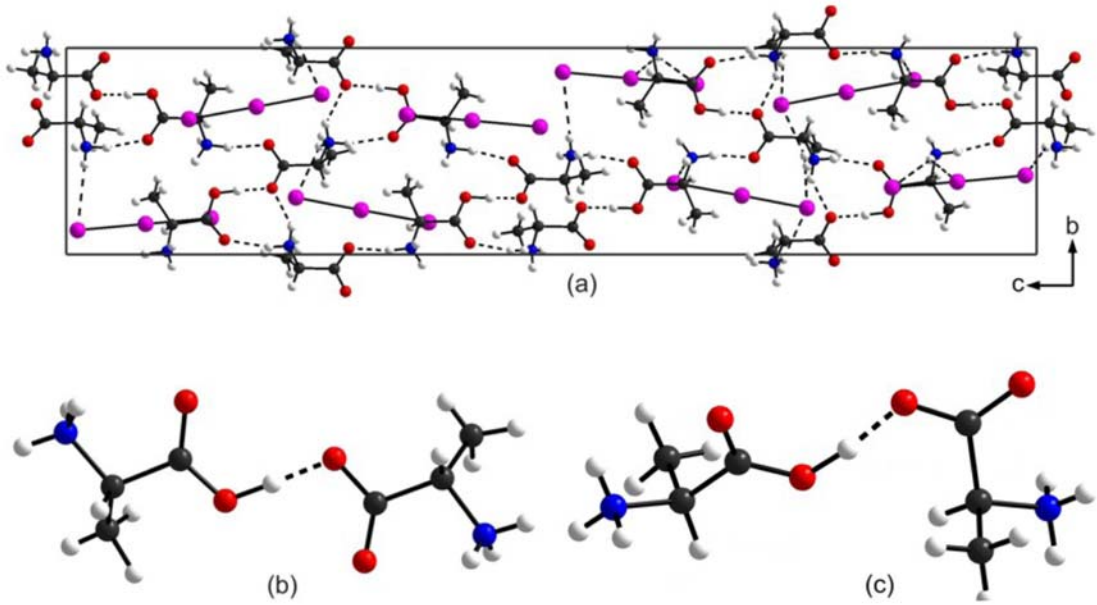


**Figure 2.** Crystal structure of (*ala*H)(*ala*$H_2$)$I_3$ (1), viewed along [100] (a). The iodine atoms are shown as large, carbon, oxygen, nitrogen as medium and hydrogen atoms as small spheres. Hydrogen bonds are indicated by dashed lines. In the detail (b), the very strong hydrogen bond between the alaninium molecule (left) and the alanine molecule (right) is shown, as compared to the respective dimer in (*ala*H)(*ala*$H_2$) nitrate[17] (c).

All other hydrogen bonds within the structure, extending from the amino groups to oxygen or iodine atoms, are of a weaker nature (see Table 4).

## 3. 2. Structure of Alanine Strontium Chloride Trihydrate, $(C_3H_7NO_2)$ $SrCl_2 \cdot 3H_2O$ (2)

The atomic arrangement in compound (2) is characterised by chains of large, irregular $[SrO_7Cl]$-polyhedra.

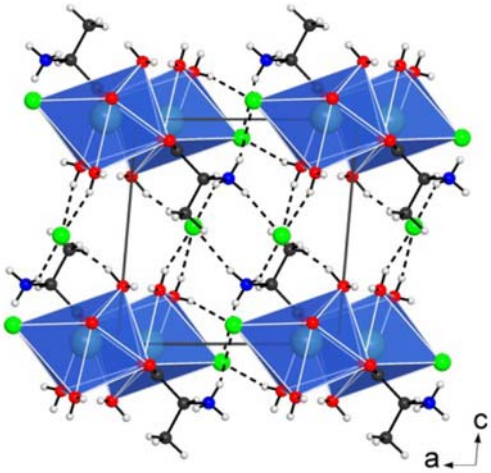


**Figure 3.** Crystal structure of (*ala*H) $SrCl_2 \cdot 3H_2O$ (2), viewed along the polyhedral chains parallel [010]. Note the two different chloride ions, one as part of the coordination sphere, another in the interstices.

The Sr–O-distances (Table 3) within each polyhedron range from 2.521(2) to 2.849(2) Å, the Sr–Cl-distance is 2.8910(9) Å. Each polyhedron shares a common face (defined by four oxygen atoms) with another to one side and a common edge (defined by two oxygen atoms) to another on the opposing side, thus forming zig-zag chains along [010] (Fig. 3). The alanine molecules adapt the roles of both bidentate and bridging ligands and face away from the chain axis (more or less perpendicular, the C–C–C-plane is nearly parallel (010)). Adjacent chains are connected to sheets parallel (001) by hydrogen bonds, further hydrogen bonds involving another, non-coordinating chloride ion located in the interstices, connect these to a three-dimensional framework.

Similar arrangements are found in (*ala*H) $MnCl_2$ $2H_2O$,[18] which is also composed of chains, albeit of smaller $[MnO_5Cl]$-polyhedra which share common corners, and in(*ala*H) $\cdot$ $CdCl_2$,[27] whose crystal structure is characterised by chains of edge-sharing $[CdCl_4O_2]$-polyhedra (Fig. 4). This topology – condensed polyhedra with (O,O)- and (O,O')-bridging carboxylate ligands is also found in related glycine compounds, e.g. (*gly*H)$_2$$SrCl_2$ $3H_2O$ and (*gly*H)$_2$$BaCl_2$ $H_2O$.[28]

Not all compounds of alanine with inorganic salts feature chain structures. For instance, in (*ala*H)$_2$ $HoCl_3$ $4H_2O$[29] there are linked dimers of polyhedra, similar in topology as in the family of (*gly*H)$_2$ $\times$ $MX_2$ $\cdot$ n$H_2O$ compounds(for $M$ = $Cr^{II}$, $Mo^{II}$; $X$ = Cl, Br; n = 1.5, 2)[30–31] in which the amino acid molecules act as bridging ligands.

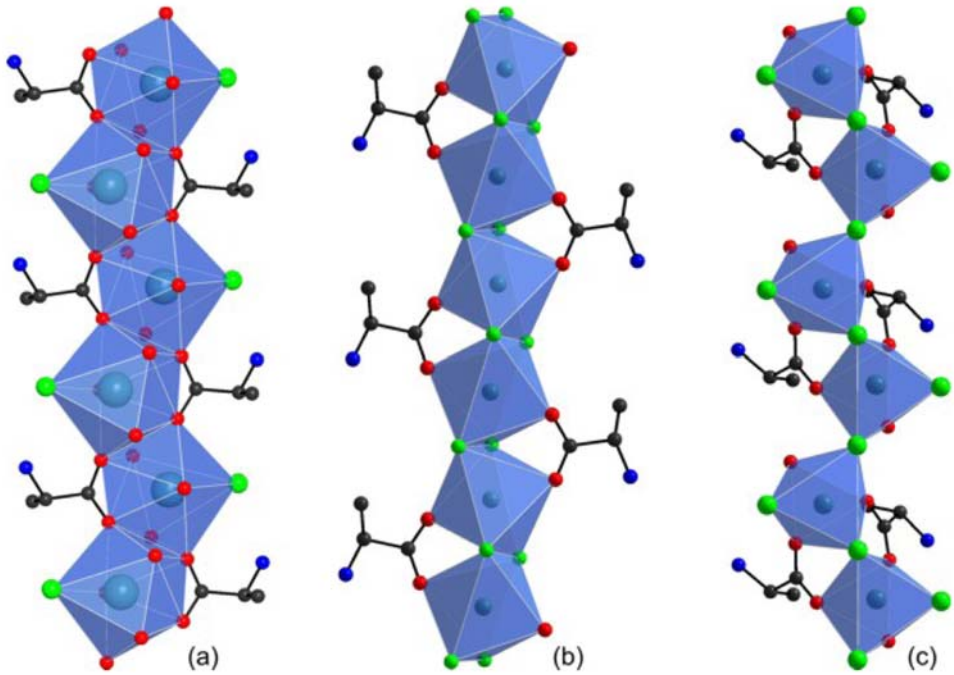


**Figure 4.** Polyhedral chains in alanine metal chloride compounds: Chains of face-sharing polyhedra parallel [010] in (*ala*H) $SrCl_2 \cdot 3H_2O$, chains of edge-sharing polyhedra parallel [010] in (*ala*H) $CdCl_2$[27] and chains of corner-sharing polyhedra parallel [100] in (*ala*H) $MnCl_2 \cdot 2H_2O$.[18] Hydrogen atoms are omitted for clarity.

There is one more alanine compound that has related glycine counterpart, *viz*. (*ala*H)$_2$ · $Pt^{II}Cl_2$[32] and (*gly*H)$_2$$Pt^{II}Cl_2$,[33] in which there are planar [4]-coordinate Pt atoms with two chloride and two N-monodentate amino acid ligands (Fig. 5).

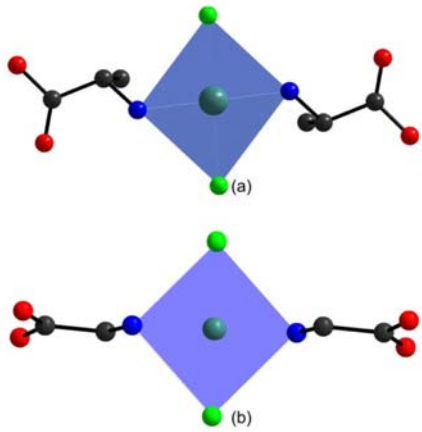


**Figure 5.** The similar coordination system in (*ala*H)$_2$ $Pt^{II}Cl_2$[31] (a) and (*gly*H)$_2$$Pt^{II}Cl_2$[32] (b), hydrogen atoms are omitted for clarity. Site symmetries are 2 and –1, respectively.

Only for L-alanine itself, thermal expansion along *a* and *b* was reported, [34] a following study found extraordinary negative thermal expansion along *c*.[35]

## 3. 2. Stability Range

A simultaneous thermogravimetric and DTA investigation of (1) with a heating rate of 5 K min$^{-1}$ (Fig 6) recorded an onset of the decomposition approximately at 395K. With increasing temperature a strong endothermic DTA signal at 428K indicates the melting of the sample (Fig. 6).

## 3. 3. Thermal Expansion

The tensor of thermal expansion [$\alpha_{ij}$] in orthorhombic crystals possesses three independent components $\alpha_{11}$, $\alpha_{22}$ and $\alpha_{33}$. The components are related to a Cartesian coordinate system $\{\vec{e}_i\}$ with $\vec{e}_1$, $\vec{e}_2$, $\vec{e}_3$, parallel to the crystallographic axes $\vec{a}$, $\vec{b}$, $\vec{c}$, respectively. With the knowledge of the stability range of the compound we determined the temperature dependence of lattice constants in the temperature range from 298 K to 383 K using high-resolution variable-temperature X-ray powder diffraction.

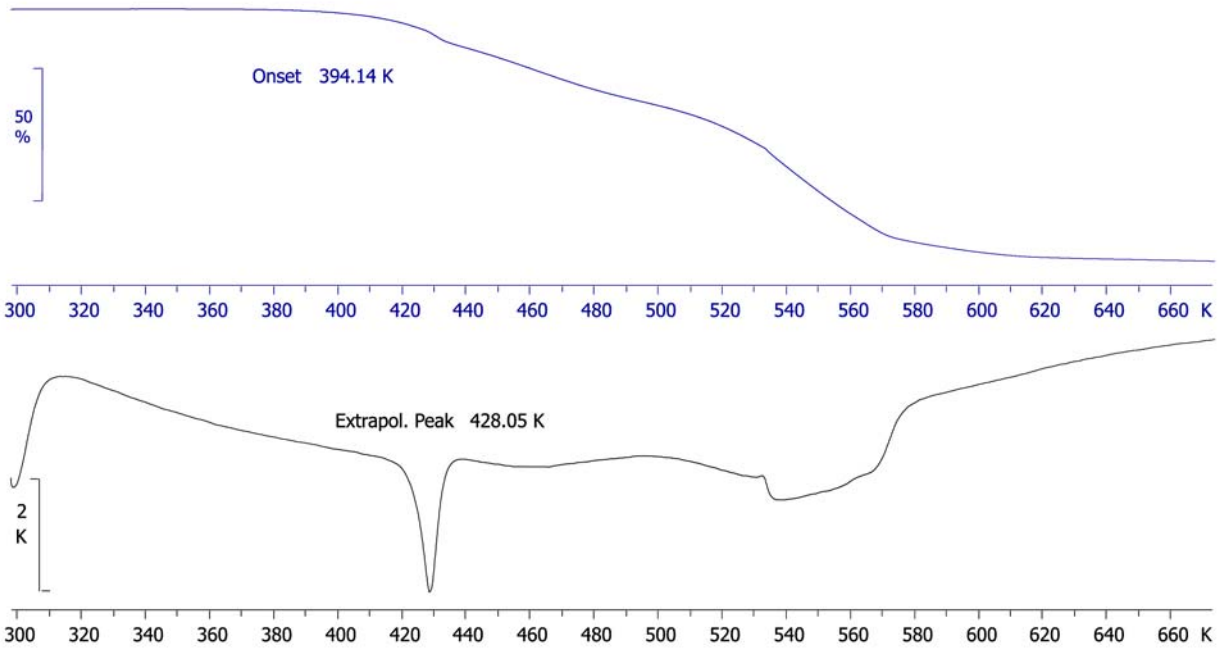


**Figure 6.** Plot of the thermal analysis of (1) with the TGA signal and the calculated onset (upper curve), and the DTA signal with the extrapolated endothermic peak (lower curve). Used sample weight 21.92 mg.

## 3. 1. Thermal Properties of (*ala*H)(*ala*H$_2$)I$_3$

Despite being of interest in possible applications, data about the thermal expansion on compounds of amino acids with inorganic salts or acids still remain limited.

In Table 5 the measured cell parameters as function of temperature are given. Since no structural phase transitions were observed in the investigated temperature range the measured data could be fitted using a regression polynominal of the general type

$$L(T–T_0) = L^0 [1 + A(T–T_0) + B(T – T_0)^2 + + C(T – T_0)^3 + \dots ] = L^0 [1 + A\tau + B\tau^2 + + C\tau^3 + \dots] \quad (1)$$

Here $L^0$ is the lattice constant *a* or *b* or *c* at $T_0$ (in our case 298 K, which corresponds to $\tau = 0$).

A polynomial of third rank proved to be sufficient for an adequate description of the observed temperature-dependent changes in lattice constants (Fig. 7):

$$a\ (T) = 8.3683\ [1 + 66.04 \times 10^{-6}\,(T – 298) – 0.092 \times \times 10^{-7}\,(T – 298)^2 – 1.42 \times 10^{-9}\,(T – 298)^3]$$

$$(\chi^2 = 5.5 \times 10^{-9})$$

$$b\ (T) = 8.9118\ [1 + 59.07 \times 10^{-6}(T – 298) + 1.02 \times \times\ 10^{-7}\,(T – 298)^2 – 2.44 \times 10^{-9}\,(T – 298)^3]$$

$$(\chi^2 = 5.8 \times 10^{-9})$$

$$c\ (T) = 41.877\ [1 + 22.11 \times 10^{-6}(T – 298) – 2.59 \times \times\ 10^{-7}\,(T – 298)^2 + 1.53 \times 10^{-9}\,(T – 298)^3]$$

$$(\chi^2 = 8.0 \times 10^{-10})$$

($\chi^2$ is the square of the residuals of the polynominal fit)

The coefficients of thermal expansion as a function of temperature were calculated from the first derivative of these fitting polynominals divided by the initial lattice constants $L^0$:

$$\alpha_{ii}(\tau) = \frac{1}{L_i^0}\frac{dL_i(\tau)}{d\tau} = A + 2B\tau + 3C\tau^2 + 4D\tau^3 + \dots \quad (2)$$

At 298 K the values of the thermal expansion coefficients amount:

$\alpha_{11} = 66(9) \times 10^{-6}\ K^{-1}$

$\alpha_{22} = 59(9) \times 10^{-6}\ K^{-1}$

$\alpha_{33} = 22(4) \times 10^{-6}\ K^{-1}$

The given standard deviations are calculated from the squares of the residuals of the polynominal fits. The marked anisotropy of the thermal expansion of (*ala*H)(*ala*$H_2$)$I_3$ is illustrated in Figure 8 using a representation surface with $\alpha'_{11} = \sum_i \sum_j u_{1i}u_{1j}\alpha_{ij}$ as radius vector for all directions $\vec{e}'_1 = \sum_i u_{1i}\vec{e}_i$ in space ($u_{1i}$ are directional cosines of $\vec{e}'_1$). The thermal expansion shows approximately rotational symmetric behaviour with respect to the *c* axis ($\alpha_{11} \approx \alpha_{22} \approx 3\alpha_{33}$), the minimal expansion (along the *c* direction) corresponds to the orientation of the triiodide anions $I_3^-$.

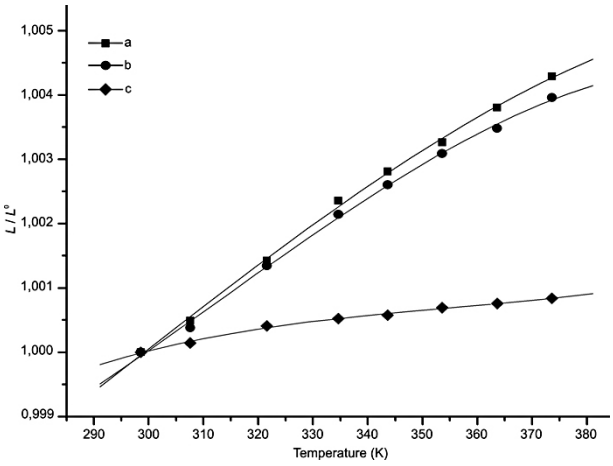


**Figure 7.** Thermal expansion of (*ala*H)(*ala*$H_2$)$I_3$ (1) as a function of the temperature. Regression curves have been fitted by third order polynomial functions. *L* is the lattice constant *a* or *b* or *c* at $(T – T_0)$, $L^0$ is the lattice constant *a* or *b* or *c* at $T_0$ (in our case 298 K).

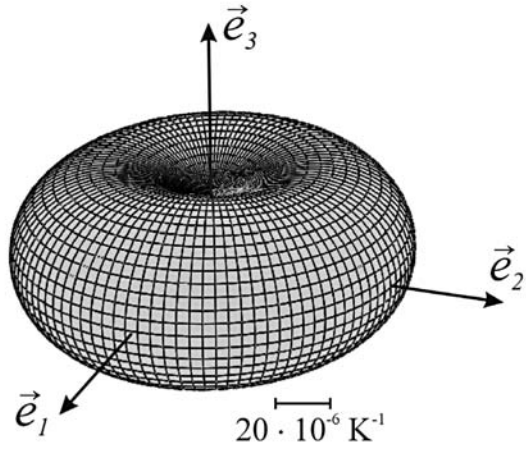


**Figure 8.** Representation surface of thermal expansion of (*ala*H)(*ala*$H_2$)$I_3$, taking $\alpha'_{11} = \sum_i \sum_j u_{1i}u_{1j}\alpha_{ij}$ as radius vector for all directions $\vec{e}'_1 = \sum_i u_{1i}\vec{e}_i$ in space ($u_{1i}$ are directional cosines of $\vec{e}'_1$).

**Table 5.** Measured cell parameters of (1) as function of temperature.

| T [K] | *a* [Å] | *b* [Å] | *c* [Å] | *V* [Å$^3$] |
|---|---|---|---|---|
| 298(1) | 8.3683(6) | 8.9118(8) | 41.877(3) | 3123.0(5) |
| 307(1) | 8.3724 | 8.9152 | 41.883 | 3126.2 |
| 321(1) | 8.3802 | 8.9238 | 41.894 | 3133.0 |
| 334(1) | 8.3880 | 8.9309 | 41.899 | 3138.8 |
| 343(1) | 8.3918 | 8.9350 | 41.901 | 3141.8 |
| 353(1) | 8.3956 | 8.9393 | 41.906 | 3145.1 |
| 363(1) | 8.4001 | 8.9428 | 41.910 | 3148.3 |
| 373(1) | 8.4042 | 8.9471 | 41.912 | 3151.5 |
| 383(1) | sample molten | | | |

# 4. Conclusions

Although at present the variety of known compounds of L-alanine with inorganic constituents does not reach that of glycine[2], a large number of such complexes can be expected. Moreover, in contrast to glycine, L-alanine compounds are necessarily non-centrosymmetric, which is a prerequisite for a number of physical effects some of which have been proven to be of interest for amino acid compounds.[3,36,37] Additionally, no two of the structurally known L-alanine compounds are isotypic, which is an indication for the chemical and conformational flexibility of alanine when combined with inorganic compounds. With this paper we have enlarged the arsenal of such L-alanine compounds by crystallographic data of two novel crystals and, in addition, investigated the thermal proerties of (*ala*H)(*ala*$H_2$)$I_3$.

# 5. Acknowledgements

The authors wish to thank Professor P. Becker (Cologne) for calculation of the representation surface (Fig. 8), and the International Center for Diffraction Data for financial support of this work (Grant 90-03 ET).

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## Povzetek

Sintetizirani sta bili dve novi spojini z L-alaninom: alanin alaninijev trijodid (1), $P2_12_12_1$, a = 8.366(2) Å, b = 8.912(2) Å, c = 41.889(8) Å and alanine·$SrCl_2 \cdot 3H_2O$ (2), $P2_1$, a = 8.540(2) Å, b = 7.167(1) Å, c = 8.769(2) Å, β = 95.02(3)°. Njuni strukturi sta bili določeni z rentgensko strukturno analizo na monokristalih. V spojini (1) so zelo močne vodikove vezi med alaninom, alaninijevim kationom in trijodidom, v spojini (2) pa so neskončne cik-cak verige [$SrO_7Cl$] z molekulami alanina in kloridnimi ioni v vmesnih prostorih. Študirana je bila tudi termična obstojnost obeh spojin.