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X-ray studies on crystalline complexes involving amino acids and peptides. XLI. Commonalities in aggregation and conformation revealed by the crystal structures of the pimelic acid complexes of L-arginine and DL-lysine

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The complexes of L-arginine and DL-lysine with pimelic acid are made up of singly positively charged zwitterionic amino acid cations and doubly negatively charged pimelate ions in a 2:1 ratio. In both structures, the amino acid molecules form twofold symmetric or centrosymmetric pairs that are stabilized by hydrogen bonds involving α-amino and α-carboxylate groups. In the L-arginine complex, these pairs form columns along the shortest cell dimension, stabilized by intermolecular hydrogen bonds involving α-amino and α-carboxylate groups. The columns are connected by hydrogen bonds and water bridges to give rise to an amino acid layer. Adjacent layers are then connected by pimelate ions. Unlike molecular ions aggregate into alternating distinct layers in the DL-lysine complex. In the amino acid layer, hydrogen-bonded lysinium dimers related by a glide plane are connected by hydrogen bonds involving α-amino and α-carboxylate groups into head-to-tail sequences. Interestingly, the aggregation pattern observed in L-arginine hemipimelate monohydrate is very similar to those in DL-arginine formate dihydrate, DL-arginine acetate monohydrate and L-arginine hemiglutarate monohydrate. Similarly, the aggregation of amino acid molecules is very similar in DL-lysine hemipimelate 0.53-hydrate, DL-lysine formate and DL-lysine hydrochloride. The complexes thus demonstrate how, in related structures, the effects of a change in composition, and sometimes even those of reversal in chirality, can be accommodated by minor adjustments in essentially the same aggregation pattern. It also transpires that the conformation of the argininium ion is the same in the four argininium complexes; the same is true about the conformation of the lysinium ion in the three lysinium complexes. This result indicates a relation between, and mutual dependence of, conformation and aggregation.

1. Introduction

The X-ray analysis of crystalline complexes involving amino acids and peptides being pursued in this laboratory (Vijayan, 1988; Part XL of this series: Saraswathi & Vijayan, 2002) was originally designed to elucidate, at atomic resolution, the geometric features of non-covalent interactions that are important in the structure, assembly and function of proteins (Bhat & Vijayan, 1976, 1977). Subsequently, the aggregation of amino acids in these complexes was found to have implications for chemical evolution (Vijayan, 1980). Much of the programme has since been used specifically to explore the role of aggregation and interactions in chemical evolution and the origin of life, with particular reference to prebiotic polymerization, chiral discrimination and self-assembly (Vijayan,

1988). For over a decade, the focus of the programme has been on complexes of amino acids with carboxylic acids that are believed to have existed in the prebiotic milieu. These studies have brought out aspects that are of considerable interest in relation to the current excitement in supramolecular association. The results of work involving monocarboxylic acids, such as formic acid (Suresh & Vijayan, 1995*a*), acetic acid (Suresh, Prasad & Vijayan, 1994) and glycolic acid (Suresh & Vijayan, 1996), were interesting, but the variety of aggregation and interaction patterns, often resulting from different juxtapositions of a few basic, relatively invariant, supramolecular elements, found full expression when dicarboxylic acids were used for complexation. The dicarboxylic acids used so far include oxalic (Chandra *et al.*, 1998), malonic (Saraswathi & Vijayan, 2002), succinic (Prasad & Vijayan, 1993), maleic (Pratap *et al.*, 2000) and glutaric (Saraswathi & Vijayan, 2001) acids. We report here the first amino acid complexes with pimelic acid, the largest dicarboxylic acid used in the programme on complexes.

2. Experimental and structure analysis

Crystals of the L-arginine complex were obtained by the diffusion of methanol into an aqueous solution of L-arginine (Sigma) and pimelic acid (AR, E-Merck) in a 1:3 molar ratio. DL-Lysine (Sigma) and pimelic acid mixed in 1:1 molar ratio were used to grow crystals of the DL-lysine complex, with ethanol as the precipitant. Extensive attempts to crystallize the respective DL-arginine and L-lysine complexes were not fruitful. Crystal data, details of data collection and refinement statistics are given in Table 1.[1] In the L-arginine complex, the water H atoms were refined isotropically, while the other H atoms were fixed geometrically and refined using a riding model. Non-H atoms were refined anisotropically. The refinement of the DL-lysine complex was bedevilled by disorder. One of the atoms (C14) in the pimelate ion has two positions, with occupancies of 0.57 and 0.43, and these two positions are only 0.504 Å apart. Only the atom with the higher occupancy is used in the discussion. Residual density between ribbons of pimelate ions (see later) posed a more serious problem. Several disordered models, each consisting of a few disordered positions, could be constructed, and the model that appeared least unsatisfactory was finally adopted. This model has two water O atoms with occupancies of 0.4 and 0.13 and an ethanol molecule with an occupancy of 0.2. This disorder is perhaps a reflection of the relative looseness of the structure. The abnormally low calculated density of the complex also indicates loose packing (density could not be measured because of the paucity of the crystals), which is possibly responsible for the low accuracy of the structure determination. No attempt was made to fix the positions of the H atoms belonging to disordered water and ethanol molecules.

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE0021). Services for accessing these data are described at the back of the journal.

Table 1
Experimental details.

	L-Arginine complex	DL-Lysine complex
Crystal data		
Chemical formula	$C_6H_{15}N_4O_2^+\cdot 0.5C_7H_{10}O_4^{2-}\cdot H_2O$	$C_6H_{15}N_2O_2^+\cdot 0.5C_7H_{10}O_4^{2-}\cdot 0.2C_2H_6O\cdot 0.53H_2O$
M_r	544.62	242.48
Cell setting, space group	Monoclinic, *C*2	Monoclinic, *C*2/*c*
a, *b*, *c* (Å)	30.278 (7), 5.1414 (12), 19.355 (5)	32.811 (17), 11.012 (6), 8.552 (4)
β (°)	115.776 (7)	91.333 (9)
V (Å^3)	2713.2 (12)	3089 (3)
Z	4	8
D_x (Mg m^{-3})	1.333	1.044
Radiation type	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	1100	950
θ range (°)	2.5–26.0	2.0–26.4
μ (mm^{-1})	0.11	0.08
Temperature (K)	293 (2)	293 (2)
Crystal form, colour	Plate, colourless	Plate, colourless
Crystal size (mm)	0.42 × 0.07 × 0.06	0.72 × 0.21 × 0.04
Data collection		
Diffractometer	Bruker SMART CCD area detector	Bruker SMART CCD area detector
Data collection method	ω–2θ	ω–2θ
No. of measured, independent and observed reflections	14 507, 3097, 2863	12 142, 3160, 2244
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.025	0.035
θ_{max} (°)	26.4	26.4
Range of *h*, *k*, *l*	$-37 \Rightarrow h \Rightarrow 37$ $-6 \Rightarrow k \Rightarrow 6$ $-23 \Rightarrow l \Rightarrow 23$	$-40 \Rightarrow h \Rightarrow 40$ $-13 \Rightarrow k \Rightarrow 13$ $-10 \Rightarrow l \Rightarrow 10$
Refinement		
Refinement on	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.039, 0.094, 1.23	0.069, 0.232, 1.12
No. of reflections	3097	3160
No. of parameters	359	190
H-atom treatment	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0414P)^2 + 0.6691P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1281P)^2 + 2.548P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	<0.0001	<0.0001
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.19, –0.15	0.49, –0.25
Absolute structure	Flack (1983)	–
Flack parameter	−10 (10)	–

Computer programs: *SMART* and *SAINT* (Bruker, 1998), *SHELXS*97 (Sheldrick, 1997), *SHELXL97* (Sheldrick, 1997), *ORTEP*-3 *for Windows* (Farrugia, 1997), *MS WORD XP*, *PLATON* (Spek, 2003).

The other H atoms were fixed and refined using a riding model.

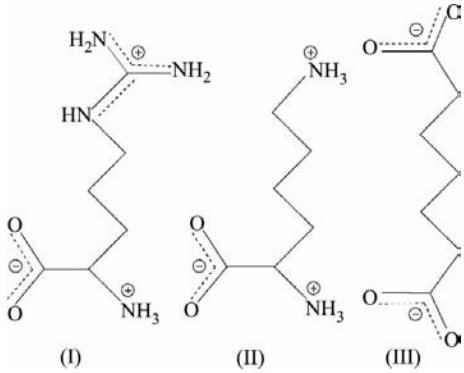
3. Results and discussion

In both structures, the pimelate ions (III) are doubly negatively charged, with deprotonated carboxyl groups at the termini. In the L-arginine complex, the pimelate ions are

Table 2
Torsion angles (°) that define molecular conformation.

L-Arginine complex		
Argininium *A*	N1—C2—C1—O1 (ψ^1)	−33.5 (3)
	N1—C2—C3—C4 (χ^1)	−179.1 (2)
	C2—C3—C4—C5 (χ^2)	−179.4 (2)
	C3—C4—C5—N6 (χ^3)	67.6 (3)
	C4—C5—N6—C7 (χ^4)	−157.9 (3)
	C5—N6—C7—N8 (χ^{51})	5.8 (4)
Argininium *B*	N11—C12 —C11—O11 (ψ^1)	−29.2 (3)
	N11—C12—C13—C14 (χ^1)	−173.7 (2)
	C12—C13—C14—C15 (χ^2)	174.9 (2)
	C13—C14—C15—N16 (χ^3)	65.8 (3)
	C14—C15—N16—C17 (χ^4)	−162.8 (3)
	C15—N16—C17—N18 (χ^{51})	5.9 (4)
Pimelate *A*	O21—C23—C24—C25	3.6 (4)
	C23—C24—C25—C26	168.8 (2)
	C24—C25—C26—C25′	−66.8 (2)
Pimelate *B*	O31—C33—C34—C35	11.5 (4)
	C33—C34—C35—C36	−168.2 (3)
	C34—C35—C36—C35′	75.3 (2)
DL-Lysine complex		
Lysininium	N1—C2—C1—O1 (ψ^1)	−31.2 (4)
	N1—C2—C3—C4 (χ^1)	−172.4 (3)
	C2—C3—C4—C5 (χ^2)	179.5 (3)
	C3—C4—C5—C6 (χ^3)	76.5 (3)
	C4—C5—C6—N7 (χ^4)	−168.7 (3)
Pimelate	O11—C13—C14*a*—C15	−13.7 (5)
	C13—C14*A*—C15—C16	−170.3 (8)
	C14*A*—C15—C16—C15′	−171.0 (8)

located on two crystallographically independent twofold axes, so that the asymmetric unit contains two half pimelate ions. The charges on these ions are compensated by the positively charged guanidyl groups of two argininium ions (I). Each arginium ion is singly positively charged, with positively charged α-amino and guanidyl groups and a negatively charged α-carboxylate group. The asymmetric unit also contains two water molecules. In the lysine complex, the dicarboxylate ion is also located on a crystallographic twofold axis, so that the asymmetric unit contains only half an ion. A zwitterionic singly positively charged lysinium ion (II) and disordered water and ethanol molecules complete the asymmetric unit.



3.1. Molecular dimensions

Perspective views of the molecules in the two structures are shown in Fig. 1, while the torsion angles that define the conformation are listed in Table 2. The two crystallographically independent argininium ions have essentially the same, somewhat folded, conformation, which is similar to that found in DL-arginine acetate monohydrate (Soman *et al.*, 1989), DL-arginine formate dihydrate (Suresh, Padmanabhan & Vijayan, 1994) and L-arginine hemiglutarate monohydrate (Saraswathi & Vijayan, 2001). The lysinium ion also has a conformation with a folded side chain *trans* to the α-amino group. The same conformation has been observed previously in DL-lysine formate (Suresh & Vijayan, 1995*b*) and DL-lysine hydrochloride (Bhaduri & Saha, 1979). The complexes described here are the first examples of doubly charged pimelate ions in crystals involving small molecules. The two arginium ions in the L-arginine complex have folded conformations, but they are folded in different ways. The pimelate ion in the DL-lysine complex has a fully extended conformation.

3.2. Molecular aggregation

The crystal structures of the two complexes are shown in Figs. 2 and 3, and the parameters of the hydrogen bonds that stabilize the structures are listed in Tables 3 and 4. The two argininium ions in the L-arginine complex are related by a pseudo-twofold axis parallel to *b*, approximately at $a = 0.75$ and $c = 0.75$, and at other locations generated from these by crystallographic symmetry. The translation involved in C-centring combines with the pseudo-twofold axis to generate a pseudo-2_1 screw axis parallel to *b* at $a = 0.5$ and $c = 0.75$, and related locations. The two pimelate ions in the structure do not have the same conformation and do not entirely obey the pseudosymmetry. However, the carboxylate groups substantially do. Thus, except for the three central C atoms in the

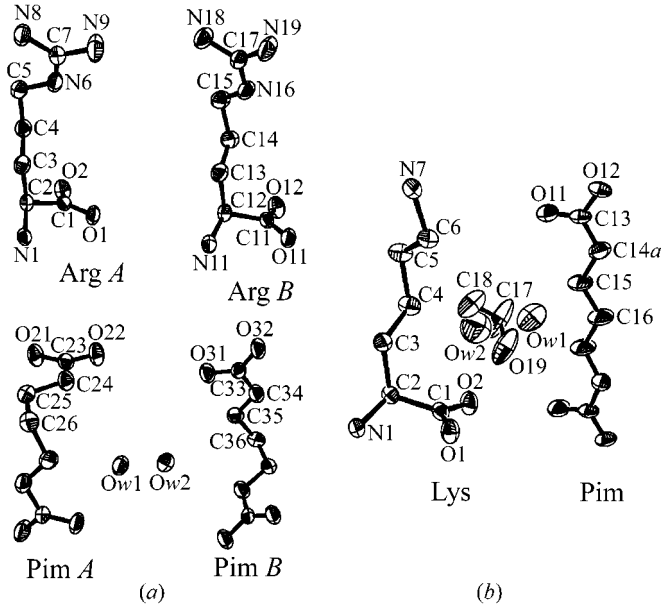


Figure 1
ORTEP diagrams of the molecular structure of (*a*) the L-arginine complex and (*b*) the DL-lysine complex. Displacement ellipsoids are shown at the 50% probability level and the atom-numbering scheme is indicated. All figures were generated using *ORTEP*-3 (Farrugia, 1997).

Table 3
Hydrogen-bond parameters in the L-arginine complex.

D—H···A	H···A (Å)	D···A (Å)	D—H···A (°)
N1—H1*a*···O2^{i}	1.89	2.770 (3)	170
N1—H1*b*···O21	1.91	2.733 (3)	152
N1—H1*c*···O11	1.91	2.781 (2)	167
N6—H6···O*w*2^{ii}	2.11	2.958 (3)	167
N8—H8*a*···O22 ^{iii}	2.01	2.834 (3)	159
N8—H8*b*···O31^{iv}	2.03	2.890 (3)	174
N9—H9*a*···O1^{iv}	2.26	2.953 (3)	138
N9—H9*b*···O32^{iv}	1.87	2.730 (4)	174
N11—H11*a*···O12^{i}	1.90	2.774 (3)	166
N11—H11*b*···O32	1.86	2.664 (3)	149
N11—H11*c*···O1	1.91	2.778 (2)	164
N16—H16···O*w*1^{v}	2.09	2.931 (3)	167
N18—H18*a*···O31^{vi}	2.15	2.878 (3)	142
N18 — H18*b*···O22^{vii}	1.85	2.710 (3)	176
N19 — H19*a*···O21^{vii}	2.05	2.914 (3)	178
N19 — H19*b*···O11^{vii}	2.18	2.926 (3)	146
O*w*1—H*w*1*a*···O12^{i}	1.91 (4)	2.721 (4)	161 (3)
O*w*1—H*w*1*b*···O*w*1^{v}	2.18 (4)	2.945 (4)	175 (5)
O*w*2—H*w*2*a*···O2^{i}	1.96 (4)	2.808 (4)	162 (3)
O*w*2—H*w*2*b*···O*w*2^{ii}	2.25 (4)	2.965 (4)	167 (4)

Symmetry codes: (i) $x, y+1, z$; (ii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+1$; (iii) $-x+1, y, -z+1$; (iv) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+1$; (v) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+2$; (vi) $-x+2, y, -z+2$; (vii) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+2$.

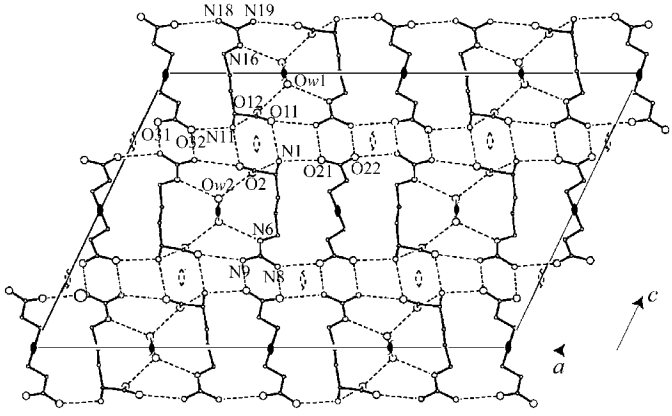


Figure 2
Crystal structure of the L-arginine complex. The pseudosymmetry elements at $a = 0.5$ and $c = 0.75$, and related locations are indicated as dotted lines.

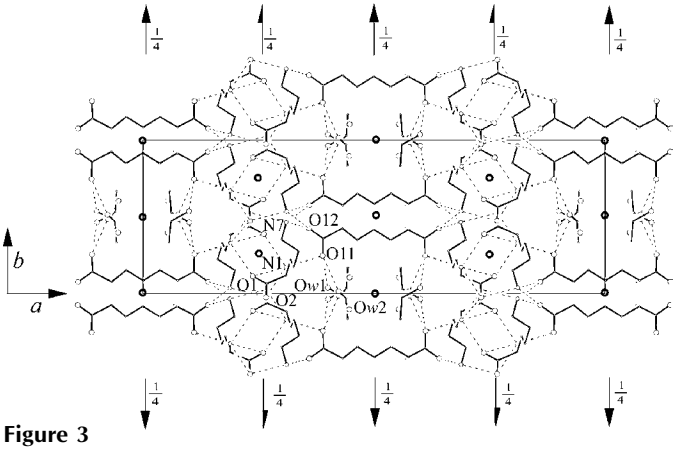


Figure 3
Crystal structure of the DL-lysine complex. For clarity, the symbols representing the glide planes have been omitted and atom O19 belonging to the disordered ethanol molecule is not numbered. All other atoms involved in hydrogen bonds are numbered.

Table 4
Hydrogen-bond parameters in the DL-lysine complex.

D—H···A	H···A (Å)	D···A (Å)	D—H···A (°)
N1—H1*a*···O1^{viii}	2.00	2.868 (3)	164
N1—H1*b*···O11^{ix}	1.89	2.769 (3)	171
N1—H1*c*···O2^{x}	1.98	2.802 (3)	154
N7—H7*a*···O2^{xi}	2.07	2.899 (3)	155
N7—H7*b*···O12^{xii}	1.95	2.817 (3)	166
N7—H7*c*···O12	1.92	2.807 (3)	173
O11···O*w*1		2.707 (12)	
O11···O19		2.790 (12)	
O*w*1···O19^{ix}		2.921 (13)	

Symmetry codes: (viii) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z$; (ix) $x, y, z-1$; (x) $x, -y, z-\frac{1}{2}$; (xi) $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (xii) $x, -y+1, z-\frac{1}{2}$.

pimelate ions, the entire structure approximately obeys the pseudo-twofold and pseudo-2_1 screw symmetries. Therefore, these pseudosymmetry elements are also taken into account in the discussion below.

In the crystal structure of the arginine complex, the argininium ions form hydrogen-bonded dimers involving N—H···O1 hydrogen bonds across the pseudo-twofold axes. The dimers stack along *b*, thus forming columns, and adjacent pairs in each column are connected through N1—H···O2 and N11—H···O12 hydrogen bonds. Each of these hydrogen bonds and their translational equivalents form what have been described as head-to-tail sequences (Suresh & Vijayan, 1983; Vijayan, 1988), in which α-amino and α-carboxylate groups of adjacent molecules are brought into periodic hydrogen-bonded proximity. The columns are stacked along *a*, thus forming an argininium layer, and interact *via* N—H···O hydrogen bonds involving the guanidyl and carboxylate groups of adjacent molecules and water bridges. The interface between adjacent columns presents an interesting arrangement in which a column of water molecules generated by a crystallographic 2_1 screw axis is trapped between two stacks of argininium ions. The water column, which interacts with both stacks, helps stabilize the argininium layer. The argininium layers are held together in the crystal by interactions involving

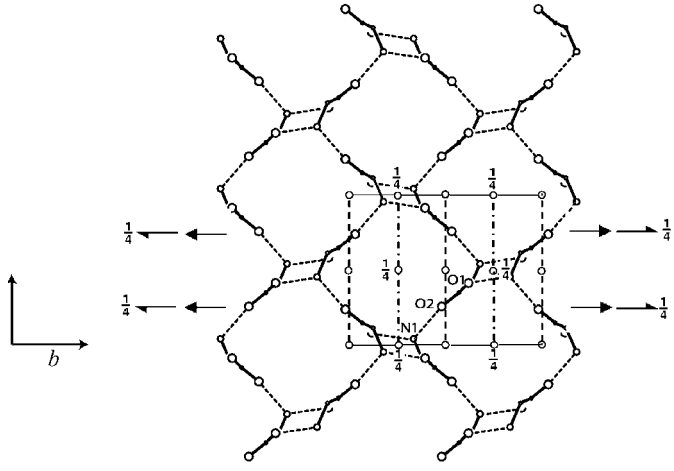


Figure 4
Lysinium layer in the DL-lysine complex. Side chains have been omitted for clarity.

the pimelate ions, but the arginine layers do not interact directly among themselves. Likewise, the pimelate ions interact only with argininium ions; in fact, each pimelate ion is surrounded by argininium ions.

As is the case for many other binary complexes involving amino acids, the unlike molecules clearly aggregate into alternating layers in the crystal structure of the DL-lysine complex (Fig. 3). The lysinium layer is stabilized primarily by interactions involving the α-amino and α-carboxylate groups (Fig. 4). The ions form hydrogen-bonded pairs across inversion centres. Each pair is stabilized by an N1—H···O1 hydrogen bond and its symmetry equivalent, and each ion in the pair is part of a head-to-tail sequence parallel to *c* and generated by an N1—H···O2 hydrogen bond between glide-related molecules and its glide equivalents. The arrangement is further stabilized by a hydrogen bond between the side-chain amino group and a carboxylate O atom of a glide-related lysinium ion. Adjacent lysinium layers are far apart and are connected by the dicarboxylate ions *via* their carboxylate groups. The carbon skeleton of the pimelate ions forms a ribbon along *c*, which makes use of the inversion centres with $a = 0.5$ and $b = 0.5$. The region between ribbons (centred around inversion centres with $a = 0.5$ and $b = 0$) contains disordered water and ethanol molecules, which connect the carboxylate groups of pimelate ions (Fig. 3).

3.3. Recurring features of aggregation and conformation

The crystal structures of DL-arginine formate dihydrate (Suresh, Padmanabhan & Vijayan, 1994), DL-arginine acetate monohydrate (Soman *et al.*, 1989) and L-arginine hemiglutarate monohydrate (Saraswathi & Vijayan, 2001) are remarkably similar to that of L-arginine hemipimelate monohydrate. There are, however, differences. One difference is that hydrogen-bonded dimerization takes place across inversion centres in the DL-arginine complexes, while it occurs across twofold axes when the L-isomer alone is involved. In spite of these differences, the aggregation pattern remains essentially the same, as is clearly seen in the arrangement of argininium ions around the carboxylate or dicarboxylate ions illustrated in Fig. 5. In all cases, the most striking feature is the pair of type *A* specific interactions (Salunke & Vijayan, 1981; Vijayan, 1988), each involving two parallel N—H···O hydrogen bonds between the guanidyl group of the argininium ion and the carboxylate group of the counter-ion. In addition, the disposition of the argininium ions that flank this feature is nearly the same in all of the structures. It is also remarkable how the gap between the specific interactions is filled. Two formate ions alone do not provide the required length, and so two water molecules must be present between the formate ions. Two acetate ions just fit, as the non-bonded distance between the two methyl groups needs to be large. A glutarate ion with an extended conformation for the carbon skeleton has the right length. The larger pimelate ion has to have a somewhat folded carbon skeleton in order to play the same role. Interestingly, the interactions between columns made up of hydrogen-bonded pairs of argininium ions, including those

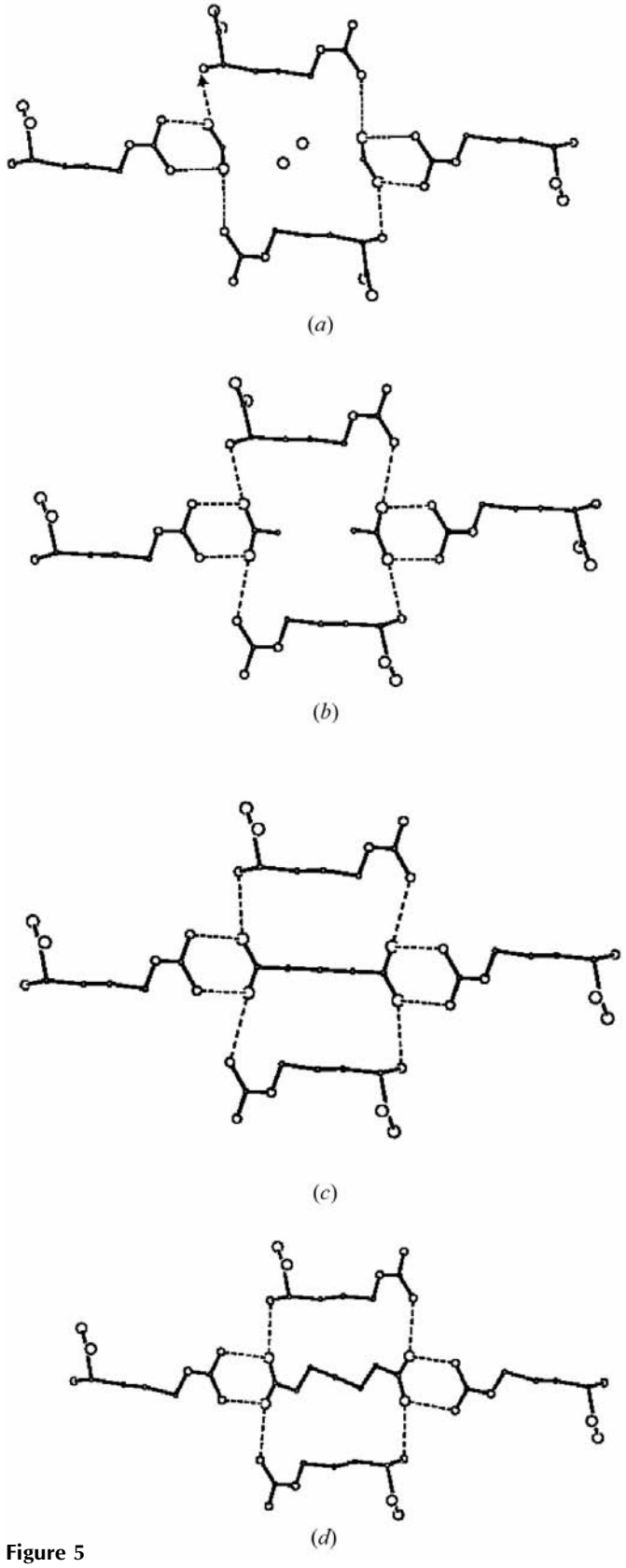


Figure 5
Disposition of argininium ions around carboxylate or dicarboxylate ion(s) in (*a*) DL-arginine formate dihydrate, (*b*) DL-arginine acetate monohydrate, (*c*) L-arginine hemiglutarate monohydrate and (*d*) L-arginine hemipimelate monohydrate. The arrow in (*a*) indicates that the hydrogen bond is not in the plane.

mediated by the water column, remain nearly the same in the four complexes. Two of the four complexes involve DL-arginine, while the remaining two contain L-arginine. However, the aggregation pattern is similar in all four, providing yet another instance where the effects of reversal of chirality of half of the molecules are accommodated by minor adjustments in essentially the same pattern.

The pattern of amino acid aggregation in DL-lysine hemipimelate monohydrate is the same as that found in DL-lysine formate (Suresh & Vijayan, 1995*b*) and DL-lysine hydrochloride (Bhaduri & Saha, 1979), and this commonality is also reflected in the unit-cell dimensions. The lysininium ions form layers parallel to the *bc* plane. The *b* axis in the three structures varies between 11.052 and 11.360 Å, while the variation in *c* is between 8.481 and 8.660 Å. The negative ions are interspersed between the lysinium layers. The role of two formate ions in the formate complex is performed by one pimelate ion in the complex involving pimelate, as the latter has two carboxylate groups. The chloride, formate and pimelate ions have different shapes and sizes, but these differences do not affect the aggregation in the amino acid layer and are only reflected in the packing of the layers interspersed with negative ions, particularly in the *c* dimension.

Arginine and lysine have long side chains that exhibit considerable conformational flexibility (Saraswathi & Vijayan, 2002; Prasad & Vijayan, 1991), and yet the argininium ion has the same conformation in the four complexes with the common aggregation pattern mentioned previously. Obviously, the same juxtaposition of the α-amino and α-carboxylate groups on the one hand and the guanidyl group on the other is necessary in order to maintain aggregation patterns of the type illustrated in Fig. 5. This juxtaposition can be achieved only when the conformation of the argininium ion is the same. Although the reason is less obvious, the conformation of the amino acid is the same in DL-lysine hydrochloride, DL-lysine formate and DL-lysine hemipimelate monohydrate, three complexes with a common pattern of amino acid aggregation. Thus, the present study provides a telling example of the relation between, and indeed the mutual dependence of, molecular conformation and molecular aggregation.

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