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X-ray studies on crystalline complexes involving amino acids and peptides. XLII. Adipic acid complexes of L- and DL-arginine and supramolecular association in arginine–dicarboxylic acid complexes

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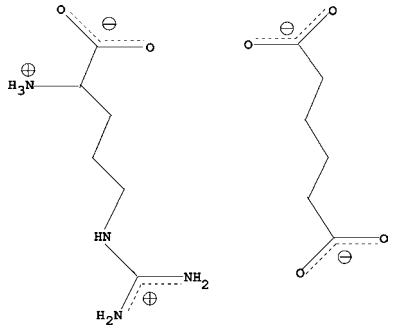
The adipic acid complexes of DL-arginine and L-arginine are made up of zwitterionic, singularly positively charged arginium ions and doubly negatively charged adipate ions, with a 2:1 stoichiometry. One of the two crystallographically independent arginium ions in the L-arginine complex has a conformation hitherto unobserved in crystal structures containing the amino acid. In the present study the structural data on arginine complexes of saturated dicarboxylic acids with 0–5 C atoms separating the two carboxyl functions are given. In terms of molecular aggregation, formic and acetic acid complexes behave in a similar way to those involving fairly long carboxylic acids such as adipic acid. By and large, the supramolecular assembly in complexes involving dicarboxylic acids with 3 or more C atoms separating the carboxyl groups (glutaric, adipic and pimelic acids), and those involving formic and acetic acids, have common features. The aggregation patterns in complexes involving oxalic, malonic and maleic acids do not share striking features among themselves (except for the mode of hydrogen-bonded dimerization of arginium ions) or with those involving larger dicarboxylic acids. Complexes of succinic acid, the shortest linear dicarboxylic acid, share features with those involving shorter as well as longer dicarboxylic acids. The difference in the behaviour of long and short dicarboxylic acids and the ambiguous behaviour of succinic acid can be broadly related to their lengths.

1. Introduction

We have been pursuing a long-range program involving the preparation and X-ray analysis of crystalline complexes of amino acids and peptides (Vijayan, 1988; Saraswathi *et al.*, 2003), among themselves as well as with molecules such as the carboxylic acids that are believed to have existed in the prebiotic milieu (Miller & Orgel, 1974; Sephton, 2002). Wherever possible, L and DL amino acid complexes were simultaneously examined to delineate chiral effects. An early observation to emerge from these studies was that in these complexes, and indeed amino acids in general, the α-amino and α-carboxylate groups are brought into periodic hydrogen-bonded proximity in a peptide-like arrangement, an arrangement that could facilitate prebiotic polymerization (Vijayan, 1980, 1988). It was also observed that chiral discrimination could be achieved through molecular interactions. In one instance, *i.e.* that involving glycolic acid, complexation led to chiral separation (Suresh & Vijayan, 1996). This is the first

time that the optical resolution of a racemic mixture could be achieved through interaction with an achiral molecule. The work on complexes also brought to light several, often predictable, specific interactions, and interaction and aggregation patterns (Salunke & Vijayan, 1981, 1983; Vijayan, 1988).



The variety in aggregation and interaction patterns, often resulting from the different juxtapositions of a few basic relatively invariant supramolecular elements, found full expression when dicarboxylic acids were used for complexation. Amino acid molecules often exhibit remarkable variation in stoichiometry, ionization state and aggregation pattern in the presence of another molecule. The variations are often also profoundly influenced by chiral effects. The complexes provide a means of exploring the conformational variability of the molecules involved. They also bring out the relation between conformation and aggregation. In addition to its considerable relevance to chemical evolution and origin of life, the work on complexes constitutes a contribution to the currently active area of supramolecular chemistry.

The dicarboxylic acids used for complexations in this laboratory include oxalic (Chandra *et al.*, 1998), malonic (Saraswathi & Vijayan, 2002), maleic (Pratap *et al.*, 2000), succinic (Prasad & Vijayan, 1993), glutaric (Saraswathi & Vijayan, 2001) and pimelic acids (Saraswathi *et al.*, 2003). The length of the carbon skeleton that separates the two carboxylic acids progressively increases in these cases. In this respect, adipic acid, used in the present study, falls between glutaric and pimelic acids. Already, many features common to different complexes have been discussed. With the present study, we are able to discern a broad picture, and the variation therein, of above-molecular associations in arginine-dicarboxylic acid complexes. An attempt is made in this paper to address this broad picture, in addition to describing the structures reported here.

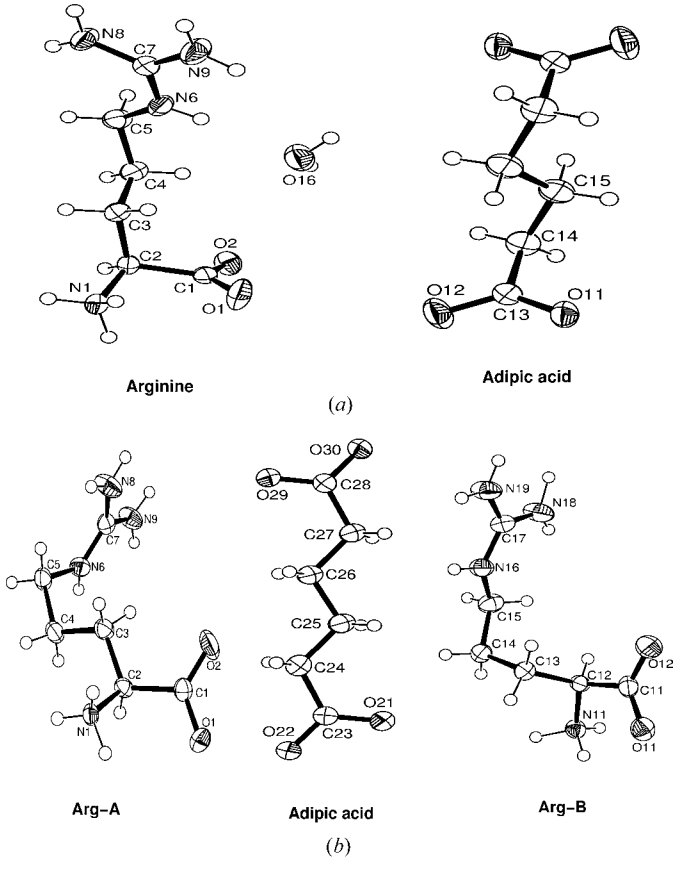


Figure 1
ORTEP diagrams of molecular structure in (*a*) the DL-arginine complex and (*b*) the L-arginine complex. The displacement ellipsoids are at the 50% probability level. The numbering scheme is indicated. All figures except Fig. 5 were generated using *ORTEP*3 (Farrugia, 1997).

2. Material and methods

Crystals of the L-arginine complex were obtained by the diffusion of ethanol into an aqueous solution of L-arginine (Sigma) and adipic acid (AR, E-Merck) that were mixed in a 1:1 molar ratio. DL-Arginine (Sigma) and adipic acid mixed in a 1:1 molar ratio were used to grow the crystals of the DL-arginine complex with isopropyl alcohol as the precipitant. Crystal data, details of data collection and refinement statistics are given in Table 1. The structures were solved by direct methods using *SHELXS*97 (Sheldrick, 1997*a*) and refined by the full-matrix least-squares method using *SHELXL*97 (Sheldrick, 1997*b*). All the H atoms in the DL-arginine complex were refined isotropically. In the case of the L-arginine complex, the H atoms were fixed using geometrical considerations and refined using the 'riding-model' method. The non-H atoms were refined anisotropically. The positional and thermal parameters of the atoms in the two structures are given as supplementary material.[1]

3. Results and discussion

3.1. Molecular dimensions

In both structures the amino acid molecules exist as positively charged zwitterionic arginium ions (I), with positively charged amino and guanidium groups, and negatively charged carboxylate groups. Both the carboxyl groups in the adipic

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE5013). Services for accessing these data are described at the back of the journal.

Table 1
Crystal data, details of data collection and refinement parameters.

	DL-Arginine complex	L-Arginine complex
Crystal data		
Chemical formula	$C_6H_{15}N_4O_2{\cdot}0.5C_6H_8O_4{\cdot}H_2O$	$2C_6H_{15}N_4O_2{\cdot}C_6H_8O_4$
M_r	265.30	494.56
Cell setting, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1$
a, b, c (Å)	13.825 (4), 5.0531 (16), 18.804 (6)	12.494 (4), 5.9510 (17), 16.719 (5)
β (°)	102.900 (6)	105.977 (5)
V (Å^3)	1280.5 (7)	1195.1 (6)
Z	4	2
D_x (Mg m^{-3})	1.376	1.374
Radiation type	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	2581	3711
θ range (°)	1.5–26.4	1.3–24.7
μ (mm^{-1})	0.11	0.11
Temperature (K)	298 (2)	298 (2)
Crystal form, colour	Plate, colourless	Platy, colourless
Crystal size (mm)	0.59 × 0.11 × 0.02	0.25 × 0.07 × 0.06
Data collection		
Diffractometer	Bruker SMART CCD area detector	Bruker SMART CCD area detector
Data collection method	φ and ω scans	φ and ω scans
Absorption correction	Multi-scan (based on symmetry-related measurements)	Multi-scan (based on symmetry-related measurements)
T_{min}	0.937	0.973
T_{max}	0.998	0.994
No. of measured, independent and observed reflections	9412, 2581, 2150	6142, 3711, 3396
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.031	0.019
θ_{max} (°)	26.4	24.7
Range of h, k, l	$-15 \Rightarrow h \Rightarrow 16$ $-6 \Rightarrow k \Rightarrow 6$ $-23 \Rightarrow l \Rightarrow 23$	$-14 \Rightarrow h \Rightarrow 14$ $-6 \Rightarrow k \Rightarrow 6$ $-19 \Rightarrow l \Rightarrow 18$
Refinement		
Refinement on	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.054, 0.128, 1.05	0.039, 0.113, 0.86
No. of reflections	2581	3711
No. of parameters	247	459
H-atom treatment	Refined independently	Refined independently
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0354P)^2 + 0.8605P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	<0.0001	0.012
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.28, −0.17	0.17, −0.17
Absolute structure	Flack (1983)	Flack (1983)
Flack parameter	Centrosymmetric	−0.1 (11)

Computer programs used: *SMART* and *SAINT* (Bruker, 2001), *SHELXS*97 (Sheldrick, 1997*a*), *SHELXL*97 (Sheldrick, 1997*b*), *ORTEP*3, *PLATON* (Spek, 1990).

acid molecule are deprotonated and negatively charged (II). Consequently, the stoichiometry between the arginium ion and the dicarboxylate ion is 2:1. The DL-arginine complex contains a water molecule while the L-arginine complex does not.

The arginine molecule (arginium ion) with its long side chain exhibits considerable conformational flexibility. The arginyl side chain in principle can assume 81 different unique conformations involving a combination of four variable torsion angles, each with three unique sterically allowed values. While not all the 81 combinations may be sterically possible, the number of allowed contributions is still likely to be large. Of these, 19 unique conformations have been observed so far (Saraswathi & Vijayan, 2002). The three crystallographically independent molecules in the two structures reported here have different conformations (Fig. 1, Table 2). Two of them have been observed earlier. The third, that of Arg B in L-arginium adipate, is observed for the first time. In this conformation, as seen in many other structures, the side chain as a whole is *trans* to the α-carboxylate group ($\chi^1 \sim -60°$). In all the structures reported until now, at least one of the two subsequent torsion angles (χ^2 and χ^3) has a value indicative of an extended *trans* arrangement. In Arg B both these angles have values ($\sim -60°$) appropriate for a *gauche* arrangement. The side chain itself therefore has a somewhat folded conformation. The adipate ion in the L-arginine complex has a fully extended conformation. The adipate conformation in the other complex is somewhat folded, although the arrangement about the central C—C bond, which primarily determines the length of the ion, is *trans*.

3.2. Crystal structure and molecular aggregation

The crystal structures of the DL and L-arginine complexes are shown in Figs. 2 and 3. The parameters of the N—H···O and O—H···O hydrogen bonds in these compounds are listed in Table 3 (and Table 4). The structure of the DL-arginine complex may be described as ribbons of alternating adipate ions and hydrogen-bonded arginium dimers along the [$\bar{1}$21] direction. The arginium ions dimerize about inversion centres. Each dimer is stabilized by an N1···O2 hydrogen bond and its centrosymmetric equivalent. Each centrosymmetric adipate ion interconnects to arginium dimers. This connectivity involves a type A specific interaction (Salunke & Vijayan, 1981; Vijayan, 1988) made up of two nearly parallel N—H···O hydrogen bonds between a guanidium group and a carboxylate group. The ribbons are then stacked along **b** to form layers parallel to the (101) plane.

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

DL-Arginine complex		
Arg	N1—C2—C1—O1 (ψ^1)	−32.3 (2)
	N1—C2—C3—C4 (χ^1)	−168.5 (2)
	C2—C3—C4—C5 (χ^2)	175.5 (2)
	C3—C4—C5—N6 (χ^3)	62.5 (2)
	C4—C5—N6—C7 (χ^4)	−161.1 (2)
	C5—N6—C7—N8 (χ^{51})	6.7 (3)
Adipate	O11—C13—C14—C15	−57.3 (3)
	C13—C14—C15—C15′	−58.1
	C14—C15—C15′—C14′	180
	C15—C15′—C14′—C13′	58.1
L-Arginine complex		
Arg A	N1—C2—C1—O1 (ψ^1)	51.4 (3)
	N1—C2—C3—C4 (χ^1)	−72.4 (2)
	C2—C3—C4—C5 (χ^2)	−169.2 (2)
	C3—C4—C5—N6 (χ^3)	64.8 (3)
	C4—C5—N6—C7 (χ^4)	−121.6 (2)
	C5—N6—C7—N8 (χ^{51})	9.1 (4)
Arg B	N11—C12—C11—O11 (ψ^1)	−25.1 (3)
	N11—C12—C13—C14 (χ^1)	−75.7 (3)
	C12—C13—C14—C15 (χ^2)	−74.6 (3)
	C13—C14—C15—N16 (χ^3)	−69.4 (3)
	C14—C15—N16—C17 (χ^4)	156.6 (2)
	C15—N16—C17—N18 (χ^{51})	−7.6 (4)
Adipic	O21—C23—C24—C25	0.1 (4)
	C23—C24—C25—C26	−177.8 (2)
	C24—C25—C26—C27	−179.6 (2)
	C25—C26—C27—C28	178.0 (2)
	C26—C27—C28—O29	4.3 (4)

Table 3
Hydrogen-bond parameters (Å, °) in the DL-arginine complex.

D—H---A	d(H···A)	d(D···A)	∠ DHA
N1—H1*A*---O12^{i}	1.82 (2)	2.742 (2)	173 (3)
N1—H1*B*---O2^{ii}	2.01 (3)	2.947 (3)	164 (4)
N1—H1*C*---O2^{iii}	1.85 (2)	2.815 (2)	178 (2)
N6—H6---O*W*16^{iv}	2.10 (3)	2.933 (3)	176 (3)
N8—H8*B*---O11^{iv}	1.90 (3)	2.809 (3)	177 (3)
N8—H8*A*---O11^{v}	2.06 (2)	2.847 (2)	165 (3)
N9—H9*A*---O12^{iv}	1.96 (3)	2.828 (3)	177 (3)
N9—H9*B*---O1^{vi}	2.14 (3)	2.885 (3)	143 (3)
O*W*16—H16*B*---O2^{vi}	1.96 (4)	2.751 (3)	166 (4)
O*W*16—H16*A*---O*W*16^{vii}	2.07 (4)	2.885 (3)	168 (3)

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

Adjacent ribbons, related by a *b* translation in each layer, are connected by N1—H···O2 hydrogen bonds. These hydrogen bonds give rise to *S*2-type head-to-tail sequences (Vijayan, 1980, 1988; Suresh & Vijayan, 1983) parallel to **b**. Adjacent layers in the crystal structure are related by 2_1 screw axes.

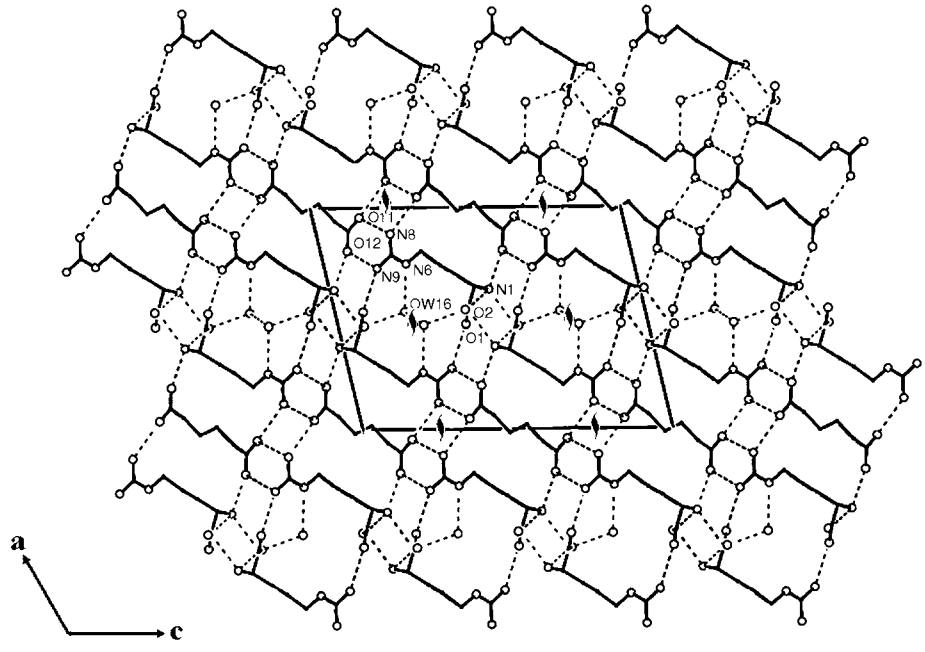


Figure 2
Crystal structure of the DL-arginine complex. In this figure and in Fig. 3, only atoms involved in N—H···O or O—H···O hydrogen bonds are numbered. The glide plane and some of the inversion centres are not indicated, for clarity.

There are direct interactions between the guanidium groups in one layer and the carboxylate groups of adipate ions in the other. Other such interactions are between the guanidium ions in one layer and the α-carboxylate groups in the other, and between the α-amino groups in one layer and adipate carboxylate groups in the other. In addition, water-mediated interactions between the guanidyl groups in one layer and the α-carboxylate groups in the other also exist. The water molecules involved in these interactions form infinite hydrogen-bonded chains around the 2_1 screw axes parallel to **b**, as in several other arginine–carboxylic acid complexes (for example, Saraswathi & Vijayan, 2002).

The two crystallographically independent amino acid molecules in the L-arginine complex are related by a pseudoinversion centre located at 0.75, 0.625 and 0.75. Such pseudoinversions also exist at points generated by one or more half-translations. The inversion centres are not exact as both the molecules have the same handedness but their conformations are different. However, the packing is such as to maximize the pseudoinversion relationship.

The molecular aggregation in the L-arginine complex has similarities to that in the DL-arginine complex. The layers made up of arginium ions interconnected by adipate ions are now parallel to the $(10\bar{1})$ plane. Ribbons of arginium dimers interconnected by adipate ions, found in the DL-arginium complex, do not occur in the L-arginine complex. Instead, the basic unit is two arginium ions interconnected by an adipate ion. The adjacent units in the layer are related by a 2_1 screw axis and are interconnected by an N—H···O hydrogen bond between the α-amino group in one and the α-carboxylate group in the other. This

Table 4
Hydrogen-bond parameters (Å,°) in the L-arginine complex.

D—H---A	d(H···A)	d(D···A) (Å)	∠ DHA
N1—H1A---O21^{i}	1.83 (2)	2.738 (3)	163 (2)
N1—H1B---O2^{ii}	1.91 (3)	2.782 (3)	175 (3)
N1—H1C---O1^{iii}	1.92 (3)	2.803 (3)	155 (2)
N6—H6A---O11^{iv}	2.15 (3)	2.970 (3)	149 (2)
N8—H8B---O30 ^{v}	1.87 (3)	2.811 (3)	164 (3)
N8—H8A---O30 ^{vi}	1.87 (3)	2.740 (3)	175 (2)
N9—H9A---O11^{iv}	2.24 (3)	3.010 (3)	141 (2)
N9—H9B---O29^{vi}	2.07 (4)	2.902 (3)	175 (3)
N11—H11B---O29^{iv}	1.92 (3)	2.743 (3)	150 (2)
N11—H11A---O12^{vii}	1.66 (3)	2.755 (3)	170 (3)
N11—H11C---O11^{v}	2.19 (3)	3.026 (3)	143 (2)
N16—H16A---O1^{iv}	2.22 (2)	3.007 (3)	160 (2)
N18—H18A---O22^{ii}	1.99 (2)	2.798 (3)	169 (3)
N18—H18B---O22^{viii}	1.69 (4)	2.731 (4)	166 (3)
N19—H19B---O1^{iv}	2.28 (3)	3.069 (3)	148 (2)
N19—H19A---O21^{viii}	2.06 (3)	2.904 (4)	171 (3)

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

hydrogen bond and its symmetry equivalents give rise to *Z*1-type head-to-tail sequences (Suresh & Vijayan, 1983; Vijayan, 1988) around the 2_1 screw axes. Another hydrogen bond of the same type connecting **b**-related arginium ions and their symmetry equivalents, giving rise to *S*2-type (Suresh & Vijayan, 1983) head-to-tail sequences, further stabilize the layer. In terms of symmetry, the basic difference between the molecular arrangements in the layers of the two structures lies in the replacement of each array of inversion centres parallel to **b** in the DL-arginine complex by a 2_1 screw axis in the L-arginine complex. In the DL complex, adjacent layers are related by a series of 2_1 screw axes. In the other complex alternate screws are replaced by pseudoinversion centres. It is the screw axes leading to water columns that are replaced by pseudoinversion centres. Water molecules are not present in the L-arginine complex.

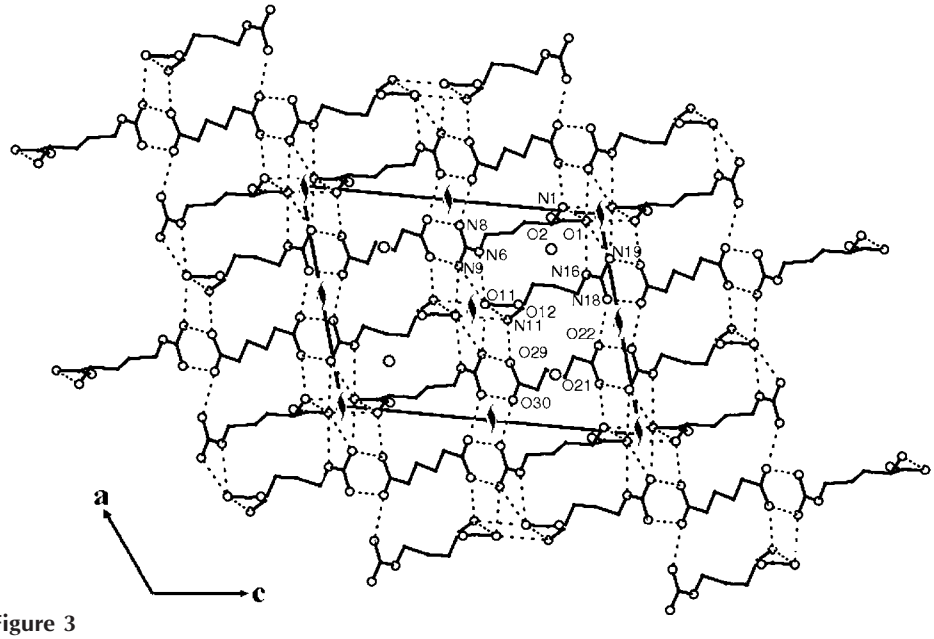


Figure 3
Crystal structure of the L-arginine complex.

4. Commonalities in supramolecular associations in arginine–dicarboxylic acid complexes

The dicarboxylic acids used in this laboratory for complexation with arginine range from oxalic acid (no C atom separating the two carboxylic groups) to pimelic acid (five C atoms between the two carboxyl groups). In every case attempts were made to prepare complexes with DL-arginine as well as L-arginine. These attempts succeeded with oxalic acid (Chandra *et al.*, 1998), malonic acid (Saraswathi & Vijayan, 2002), maleic acid (Ravisankar *et al.*, 1998), succinic acid (Prasad & Vijayan, 1990) and adipic acid. Only L-arginine complexes could be crystallized in the case of glutaric acid (Saraswathi & Vijayan, 2001) and pimelic acid (Saraswathi *et al.*, 2003). In addition, DL-arginine and L-arginine complexes of monocarboxylic formic and acetic acids have also been studied in this laboratory (Suresh *et al.*, 1994; Suresh & Vijayan, 1983; Soman *et al.*, 1989). These 16 crystalline complexes provide an ensemble of crystal structures to explore the commonalities and variation in aggregation in arginine–carboxylic acid complexes.

Most of the complexes involving long carboxylic acid molecules (3–5 C atoms separating the two carboxyl groups) and the two monocarboxylic acids exhibit aggregation patterns with similarities. The crystal structure of DL-argininium adipate monohydrate, reported here, represents a subgroup among them. Interestingly, DL-arginine acetate monohydrate and DL-arginine formate dihydrate exhibit the same aggregation pattern except that an adipate ion is replaced by two acetate ions or two formate ions and water molecules, as illustrated in Fig. 4. All the three structures have the same space group ($P2_1/c$) and similar unit-cell dimensions. A similar aggregation pattern exists in L-arginine glutarate monohydrate and L-arginine pimelate monohydrate except that the inversion centres are now replaced by crystallographic or non-crystallographic twofold axes. Also, the arginium ions now dimerize about a twofold axis with the help of an N1···O1 hydrogen bond, rather than an N1···O2 hydrogen bond, and its symmetry mate. A somewhat similar arrangement exists in L-arginine acetate monohydrate, but the twofold axes are now replaced by 2_1 screw axes. The arrangement in L-argininium adipate is similar to that in the acetate complex. The major difference between the two is

the absence of water molecules in the adipate and the consequent small rearrangements. The only structure among the arginine complexes of longish dicarboxylic acids, formic acid and acetic acid which stands out with an entirely different aggregation pattern is L-arginine formate.

The arginine complexes with shorter dicarboxylic acids show higher variability in molecular aggregation. A common feature of the complexes of DL-arginine with oxalic, malonic and succinic acids is the centrosymmetric dimeric arrangements of the antiparallel molecules, of the type illustrated in Fig. 5. The same kind of arrangement also exists in the free base. A highly distorted version of the arrangement is also seen in the L-arginine complexes of succinic acid (Prasad & Vijayan, 1993). The aggregation patterns in the DL- and L-arginine complexes of maleic acid (Ravisankar *et al.*, 1998), and the L-arginine complexes of oxalic acid (Chandra *et al.*, 1998) and malonic acid (Saraswathi & Vijayan, 2002) do not exhibit any striking common features among themselves or with other complexes.

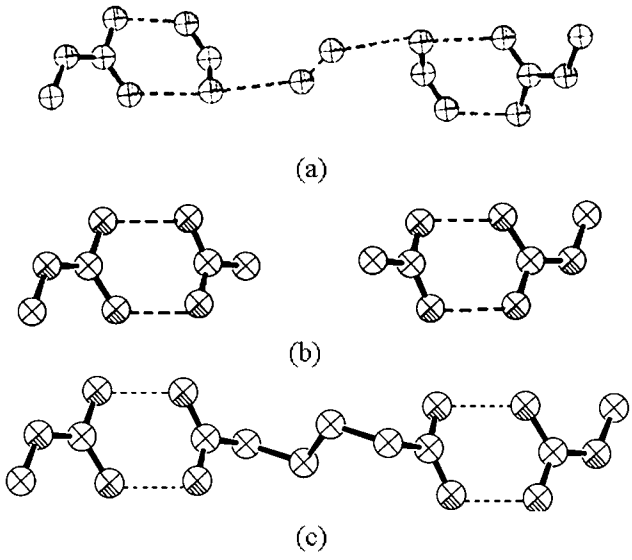


Figure 4
Basic patterns of amino acid–carboxylic acid interactions in DL-arginine (*a*) formate, (*b*) acetate and (*c*) adipate.

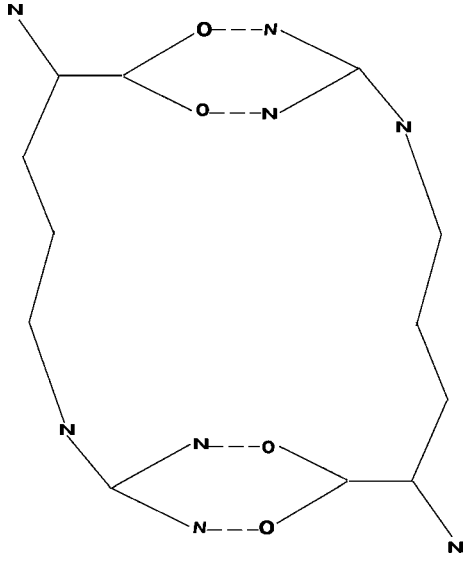


Figure 5
Schematic representation of the DL-arginine dimer involving an antiparallel arrangement.

Oxalic acid is a short, rigid molecule, as are the molecules of malonic acid and maleic acid on account of the strong internal hydrogen bond between the two carboxylic groups. On the other hand, succinic acid is a linear, flexible molecule. In fact, it is the shortest linear, flexible dicarboxylic acid molecule. Interestingly, the arginine complexes of succinic acid exhibit some, but not all, features of the complexes involving other longer, linear dicarboxylic acids. This ambiguity is also found in the observed ionization states. Oxalic, malonic and maleic acids exist as singly protonated ions in all the arginine complexes, while the longer dicarboxylic acids invariably exist as doubly charged ions in their complexes. Succinic acid exhibits all the three possible ionization states in its arginine complexes.

The above observations are perhaps related to the length of the dicarboxylic acid. The arrangement of molecules in the complexes involving the longer dicarboxylic acids is such that the arginium ions and the dicarboxylic ions lie side by side, interconnected by a hydrogen bond between a guanidyl nitrogen and a carboxylate oxygen, and by an amino nitrogen and carboxylate oxygen at the other end of the dicarboxylate ion or its symmetry equivalent in one case. The distances between the two N atoms vary between 6.25 and 6.90 Å, while those between the two O atoms are in the range 5.92–6.80 Å. Similar distances are also found between the appropriate atoms in the related formic and acetic acid complexes. These distances are appropriate for the formation of the two hydrogen bonds referred to above with a substantially linear conformation of the molecular ions. The maximum possible length between O atoms on the same side of the succinic acid molecule is *ca* 5 Å, lower than required for the formation of the two hydrogen bonds necessary for the facile occurrence of the pattern found in the complexes involving longer dicarboxylic acids. However, the length is such as to permit the retention of some features of this pattern. The geometry and size of maleic, malonic and oxalic acids are so different from those of other dicarboxylic acids that their complexes with arginine have entirely different aggregation patterns.

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