X-ray Studies on Crystalline Complexes Involving Amino Acids and Peptides. XXXIII. Crystal Structures of L- and DL-Arginine Complexed with Oxalic Acid and a Comparative Study of Amino Acid–Oxalic Acid Complexes

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Abstract

The DL- and L-arginine complexes of oxalic acid are made up of zwitterionic positively charged amino acid molecules and semi-oxalate ions. The dissimilar molecules aggregate into separate alternating layers in the former. The basic unit in the arginine layer is a centrosymmetric dimer, while the semi-oxalate ions form hydrogen-bonded strings in their layer. In the L-arginine complex each semi-oxalate ion is surrounded by arginine molecules and the complex can be described as an inclusion compound. The oxalic acid complexes of basic amino acids exhibit a variety of ionization states and stoichiometry. They illustrate the effect of aggregation and chirality on ionization state and stoichiometry, and that of molecular properties on aggregation. The semi-oxalate/oxalate ions tend to be planar, but large departures from planarity are possible. The amino acid aggregation in the different oxalic acid complexes do not resemble one another significantly, but the aggregation of a particular amino acid in its oxalic acid complex tends to have similarities with its aggregation in other structures. Also, semi-oxalate ions aggregate into similar strings in four of the six oxalic acid complexes. Thus, the intrinsic aggregation propensities of individual molecules tend to be retained in the complexes.

1. Introduction

The long-range programme based on the preparation and X-ray analysis of crystalline complexes involving amino acids and peptides, being pursued in this laboratory, has resulted in a wealth of information on molecular interactions and their consequences, which are relevant not only to present biological systems, but also to the chemical evolution and origin of life (Vijayan, 1988; Prasad & Vijayan, 1993; Suresh & Vijayan, 1996; Venkatraman et al., 1997). These results have been of considerable importance in relation to the general problem of molecular recognition and aggregation as well. The current focus of the programme has been on complexes involving small carboxylic acids, particularly those believed to have existed on the prebiotic earth (Miller & Orgel, 1974; Kvenvolden et al.,

1971). In this context the complexes containing succinic, acetic, formic and glycolic acids have already been analysed. Also determined are the structures of oxalic acid complexes of DL- and L-histidine, and lysine (Prabu et al., 1996; Venkatraman et al., 1997). Here we report the corresponding complexes of oxalic acid with DL- and L-arginine and present a comparative study of the oxalic acid complexes of basic amino acids.

2. Experimental

Crystals of the complexes were prepared by slow diffusion of ethanol and acetone into aqueous solutions of equimolar quantities of oxalic acid and L- or DL-arginine. The crystal data and the details pertaining to intensity data collection are given in Table 1. The structures were solved by direct methods using *SHELXS*86 (Sheldrick, 1985) and refined by least-squares using *SHELXL*93 (Sheldrick, 1993). The H atoms were located from difference-Fourier maps and refined isotropically in the case of the DL-arginine complex. For the L-arginine complex, the α-amino H atoms and the H atoms in the semi-oxalate ions were refined isotropically, whereas all other H atoms were fixed using geometrical considerations and refined using the 'riding-model' method (Sheldrick, 1993). Non-H atoms were refined anisotropically. Refinement statistics are given in Table 1. The final positional and equivalent isotropic displacement parameters of the non-H atoms are listed in Tables 2 and 3.†

3. Results and discussion

3.1. *Molecular dimensions*

Perspective views of the molecules in the two structures are given in Fig. 1. The arginine molecules are positively charged with protonated α-amino and guanidyl groups and de-protonated α-carboxyl groups

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† Lists of atomic coordinates, anisotropic displacement parameters and structure factors have been deposited with the IUCr (Reference: LI0261). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Experimental details*

	DL-Arginine semi-oxalate	L-Arginine semi-oxalate
Crystal data		
Chemical formula	$C_{16}H_{15}N_4O_2^+.C_2HO_4^-$	$C_6H_{15}N_4O_2^+.C_2HO_4^-$
Chemical formula weight	264.25	264.25
Cell setting	Monoclinic	Triclinic
Space group	$P2_1/c$	$P1$
a (Å)	5.1107 (12)	5.0668 (14)
b (Å)	23.937 (3)	9.7572 (13)
c (Å)	10.947 (2)	13.141 (3)
α (°)		111.11 (2)
β (°)	116.91 (2)	92.75 (2)
γ (°)		91.97 (3)
V (Å³)	1194.3 (4)	604.4 (2)
Z	4	2
D_x (Mg m⁻³)	1.470	1.452
Radiation type	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71068	0.71068
No. of reflections for cell parameters	25	25
θ range (°)	5–20	5–20
μ (mm⁻¹)	0.126	0.124
Temperature (K)	293 (2)	293 (2)
Crystal form	Needle	Needle
Crystal size (mm)	0.8 × 0.37 × 0.2	0.7 × 0.2 × 0.15
Crystal colour	Colourless	Colourless
Data collection		
Diffractometer	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4
Data collection method	ω–2θ scans	ω–2θ scans
Absorption correction	None	None
No. of measured reflections	3499	2771
No. of independent reflections	2861	2379
No. of observed reflections	2489	2084
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.0200	0.0609
θ_{max} (°)	27.97	24.68
Range of h, k, l	$0 \rightarrow h \rightarrow 6$	$0 \rightarrow h \rightarrow 6$
	$0 \rightarrow k \rightarrow 30$	$-11 \rightarrow k \rightarrow 11$
	$-14 \rightarrow l \rightarrow 12$	$-15 \rightarrow l \rightarrow 15$
No. of standard reflections	3	3
Frequency of standard reflections (min)	60	60
Intensity decay (%)	2.4	7.2
Refinement		
Refinement on	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$	0.0466	0.0343
$wR(F^2)$	0.1442	0.0968
S	1.083	1.025
No. of reflections used in refinement	2861	2379
No. of parameters used	227	349
H-atom treatment	All H-atom parameters refined	Mixed
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0778P)^2 + 0.6239P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0641P)^2 + 0.1211P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.006	−0.013
$\Delta\rho_{max}$ (e Å⁻³)	0.436	0.304
$\Delta\rho_{min}$ (e Å⁻³)	−0.482	−0.222
Extinction method	None	None
Source of atomic scattering factors	International Tables for Crystallography (1992, Vol. C)	International Tables for Crystallography (1992, Vol. C)
Computer programs		
Data collection	*CAD*-4 (Enraf–Nonius, 1989)	*CAD*-4 (Enraf–Nonius, 1989)
Cell refinement	*CAD*-4 (Enraf–Nonius, 1989)	*CAD*-4 (Enraf–Nonius, 1989)
Data reduction	Locally written software	Locally written software
Structure solution	*SHELXS*86 (Sheldrick, 1985)	*SHELXS*86 (Sheldrick, 1985)
Structure refinement	*SHELXL*93 (Sheldrick, 1993)	*SHELXL*93 (Sheldrick, 1993)

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$) for the DL-arginine complex*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
N1	0.1025 (3)	0.34333 (6)	0.72032 (13)	0.0233 (3)
O1	0.4323 (3)	0.43448 (6)	0.84495 (14)	0.0373 (3)
O2	0.7300 (3)	0.41997 (5)	0.74990 (14)	0.0327 (3)
C1	0.5010 (3)	0.41100 (6)	0.7627 (2)	0.0228 (3)
C2	0.2804 (3)	0.37020 (7)	0.65983 (15)	0.0225 (3)
C3	0.0714 (3)	0.40012 (7)	0.5286 (2)	0.0261 (3)
C4	0.2199 (4)	0.42169 (8)	0.4445 (2)	0.0303 (4)
C5	−0.0088 (4)	0.44426 (8)	0.3083 (2)	0.0288 (3)
N6	0.1130 (3)	0.46482 (7)	0.21950 (14)	0.0296 (3)
C7	0.1749 (3)	0.43299 (7)	0.1368 (2)	0.0255 (3)
N8	0.1256 (4)	0.37827 (7)	0.1271 (2)	0.0373 (4)
N9	0.2913 (3)	0.45693 (7)	0.0634 (2)	0.0306 (3)
O11	0.9038 (4)	0.19195 (8)	0.7885 (2)	0.0568 (5)
O12	0.5395 (4)	0.24654 (9)	0.77030 (15)	0.0629 (6)
C13	0.6932 (4)	0.22032 (7)	0.7221 (2)	0.0279 (3)
C14	0.5782 (4)	0.22640 (7)	0.5668 (2)	0.0288 (3)
O15	0.3916 (4)	0.19236 (6)	0.49452 (14)	0.0441 (4)
O16	0.6942 (4)	0.26418 (6)	0.52826 (13)	0.0457 (4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$) for the L-arginine complex*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
N1	0.4167 (6)	−0.0163 (3)	0.8579 (2)	0.0292 (6)
O2	−0.1958 (5)	0.0305 (3)	0.7273 (2)	0.0377 (6)
O1	0.0767 (5)	−0.1540 (3)	0.6942 (2)	0.0421 (6)
C1	0.0090 (7)	−0.0265 (4)	0.7468 (3)	0.0296 (7)
C2	0.1871 (7)	0.0674 (4)	0.8464 (3)	0.0273 (7)
C3	0.2759 (7)	0.2132 (3)	0.8389 (3)	0.0308 (7)
C4	0.4295 (8)	0.3172 (4)	0.9425 (3)	0.0372 (8)
C5	0.5307 (8)	0.4600 (4)	0.9314 (3)	0.0394 (9)
N6	0.3300 (7)	0.5333 (3)	0.8902 (2)	0.0360 (7)
C7	0.1981 (6)	0.6459 (3)	0.9496 (3)	0.0279 (7)
N8	0.1951 (7)	0.6876 (3)	1.0569 (2)	0.0399 (7)
N9	0.0681 (6)	0.7212 (3)	0.8986 (2)	0.0373 (7)
O21	0.5801 (5)	0.6817 (3)	0.7506 (2)	0.0406 (6)
O22	0.6999 (5)	0.6614 (3)	0.5860 (2)	0.0396 (6)
C23	0.5480 (7)	0.6294 (3)	0.6527 (3)	0.0289 (7)
C24	0.3176 (7)	0.5152 (4)	0.5947 (3)	0.0343 (8)
O25	0.1944 (6)	0.4665 (3)	0.6545 (2)	0.0524 (8)
O26	0.2768 (5)	0.4819 (3)	0.4941 (2)	0.0404 (6)
N11	0.7332 (7)	0.4334 (3)	0.3667 (2)	0.0336 (7)
O11	1.0380 (6)	0.2917 (3)	0.2114 (2)	0.0537 (8)
O12	1.1544 (7)	0.4876 (3)	0.1748 (3)	0.0595 (9)
C11	1.0146 (7)	0.4213 (4)	0.2169 (3)	0.0307 (7)
C12	0.7853 (7)	0.4998 (3)	0.2828 (3)	0.0284 (7)
C13	0.8306 (7)	0.6644 (4)	0.3372 (3)	0.0324 (7)
C14	0.5765 (7)	0.7445 (4)	0.3705 (3)	0.0318 (7)
C15	0.6286 (8)	0.9012 (4)	0.4498 (3)	0.0354 (8)
N16	0.8054 (7)	0.9823 (3)	0.4048 (2)	0.0349 (7)
C17	0.9233 (7)	1.1111 (3)	0.4611 (3)	0.0291 (7)
N18	0.9102 (8)	1.1748 (3)	0.5681 (2)	0.0476 (9)
N19	1.0606 (7)	1.1796 (3)	0.4096 (2)	0.0462 (8)
O32	0.3748 (6)	0.1247 (3)	0.1053 (2)	0.0436 (7)
O31	0.5177 (6)	0.1316 (3)	0.2697 (2)	0.0422 (6)
C33	0.5244 (7)	0.0840 (4)	0.1705 (3)	0.0307 (7)
C34	0.7271 (7)	−0.0295 (4)	0.1137 (3)	0.0338 (8)
O36	0.7400 (6)	−0.0591 (3)	0.0141 (2)	0.0506 (8)
O35	0.8582 (6)	−0.0800 (3)	0.1729 (2)	0.0467 (7)

in both structures. Also, oxalic acid molecules exist as negatively charged semi-oxalate ions in both structures. Arginine adopts three different conformations in the DL-arginine complex and two independent molecules in
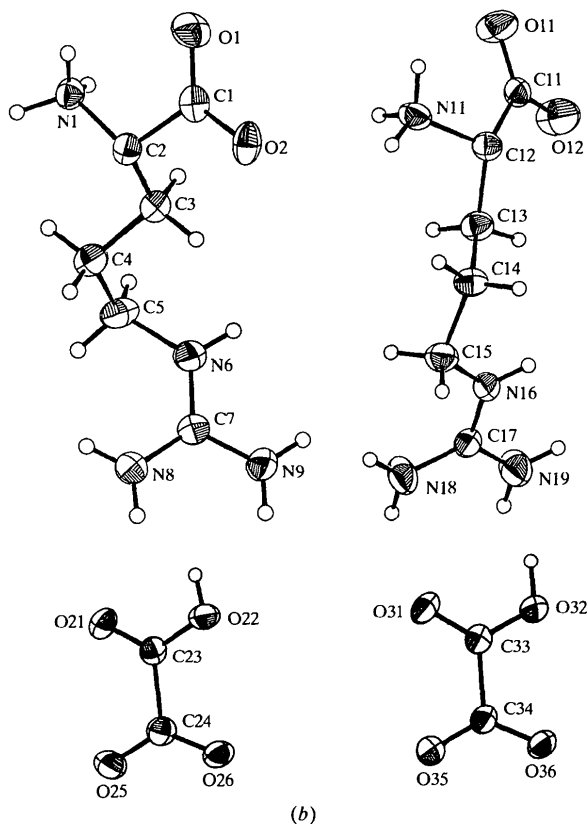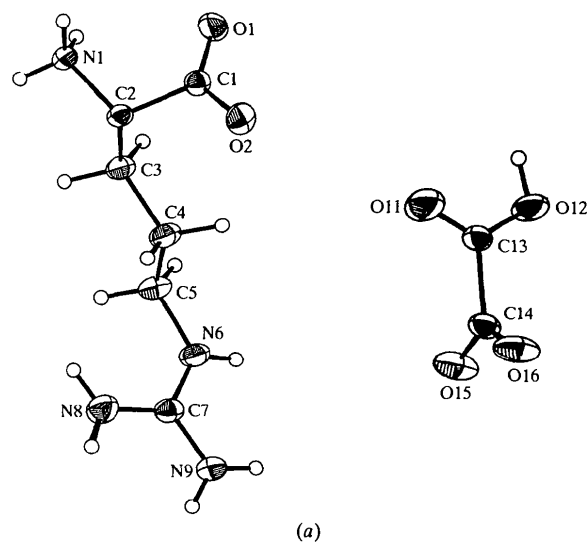

(a)

(b)

Fig. 1. *ZORTEP* diagrams (Zsolnai, 1994) of the molecules in (a) the DL-arginine and (b) the L-arginine complexes. The displacement ellipsoids are drawn at the 50% probability level. The numbering scheme is indicated. In the semi-oxalate ions, O12, O22 and O32 are protonated. H atoms are indicated as small spheres.

Table 4. *Torsion angles (°) that define the conformation of the arginine molecules in the complexes*

Compound	$\psi 1$	$\chi 1$	$\chi 2$	$\chi 3$	$\chi 4$	$\chi 5$
DL-Arginine–semi-oxalate	−30.3 (2)	−170.9 (2)	173.0 (2)	−178.8 (2)	84.0 (2)	0.9 (3)
L-Arginine–semi-oxalate						
Molecule 1	1.4 (4)	−63.9 (4)	176.7 (3)	50.1 (4)	99.4 (5)	−13.9 (6)
Molecule 2	27.4 (4)	−76.2 (4)	165.1 (4)	55.1 (4)	−167.4 (3)	6.0 (6)

the L-arginine complex (Table 4), but each is similar to one or the other 16 independent conformations observed in crystal structures of arginine and its complexes so far (Suresh *et al.*, 1994). The semi-oxalate ions in the L-arginine complex are substantially planar with the lower of the two O−C−C−O torsion angles having values of 6.1 (1) and −9.6 (1)°, whereas the semi-oxalate ion in the DL-arginine complex deviates significantly from planarity and the corresponding torsion angle is 95.2 (1)°. The carboxyl hydrogen is in the *syn* conformation with O−C−O−H angles of −7.3 (3), −0.1 (2) and 2.2 (2)° in the DL-arginine complex and the two molecules of the L-arginine complex, respectively.

3.2. Molecular aggregation

The crystal structures of the DL- and L-arginine complexes are shown in Figs. 2 and 3, while the parameters of the hydrogen bonds that stabilize them are listed in Tables 5 and 6, respectively. As in many other binary complexes involving amino acids, the unlike molecules in the DL-arginine complex aggregate into alternating layers, which stack perpendicular to the longest crystallographic axis. The arginine molecules in

the amino acid layer form centrosymmetric dimers, each dimer stabilized by two specific guanidyl–carboxylate interactions of type B (Salunke & Vijayan, 1981), as in the structure of DL-arginine hemi-succinate dihydrate (Prasad & Vijayan, 1990). Each specific interaction involves two almost parallel N−H···O hydrogen bonds. These dimers are interconnected along the shortest crystallographic axis by N1···O2 hydrogen bonds involving molecules related by translation, which give rise to S2-type head-to-tail sequences (Suresh & Vijayan, 1983). Guanidyl–carboxylate hydrogen bonds interconnect the dimers along the cell axis of intermediate dimensions. The semi-oxalate ions form strings involving glide-related molecules stabilized by O12···O16 hydrogen bonds. These strings in the layer do not directly interact among themselves. They are interconnected by arginine molecules through interactions involving the amino as well as the guanidyl groups.

The molecular aggregation in the L-arginine complex is remarkably different from that in the DL-arginine complex. The arginine molecules in the structure form a layer in the (01̄1) plane with the crystallographically independent molecules alternating along the [011] direction. One set of molecules form an S2-type head-to-tail sequence (Suresh & Vijayan, 1983) along a involving the N1···O2 hydrogen bond and its translational equivalents, while the other does not. The guanidyl–carboxylate hydrogen bonds N8···O12 and N18···O2 and their translational equivalents hold together the two sets of crystallographically independent molecules in the layer. There are no direct inter-
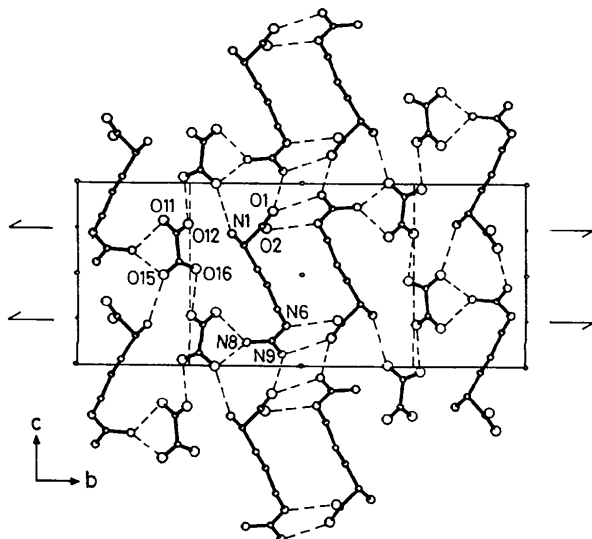

Fig. 2. Crystal structure of the DL-arginine complex. In this and the subsequent figures, O, N and C atoms are indicated by circles of decreasing size and hydrogen bonds by broken lines. Only atoms which form hydrogen bonds are labelled.
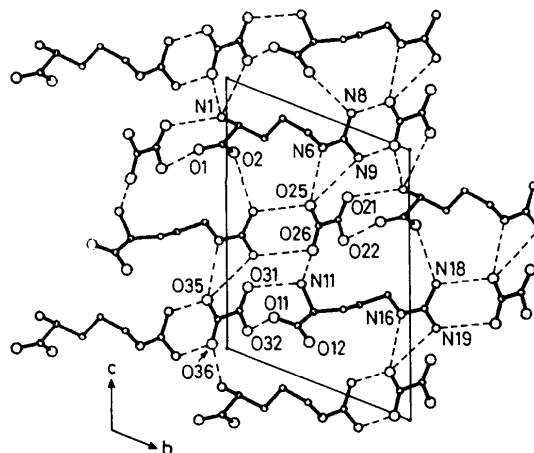

Fig. 3. Crystal structure of the L-arginine complex.

Table 5. *Hydrogen-bonding parameters (Å, °) in the crystal structure of DL-arginine semi-oxalate*

$D-H\cdots A$	$D\cdots A$	$H-D\cdots A$
N1—H1A$\cdots$O15^{i}	2.812 (2)	10 (2)
N1—H1B$\cdots$O16^{ii}	2.897 (2)	6 (2)
N1—H1C$\cdots$O2b^{ii}	2.766 (2)	3 (2)
N6—H6$\cdots$O2^{iii}	2.849 (2)	8 (2)
N8—H8A$\cdots$O15^{iv}	2.932 (3)	8 (2)
N8—H8B$\cdots$O11^{v}	3.008 (3)	6 (2)
N9—H9A$\cdots$O1^{vi}	2.844 (3)	24 (2)
N9—H9B$\cdots$O1^{iii}	2.911 (3)	12 (2)
O12—H12$\cdots$O16^{i}	2.578 (2)	10 (3)

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

Table 6. *Hydrogen-bonding parameters (Å, °) in the crystal structure of L-arginine semi-oxalate*

$D-H\cdots A$	$D\cdots A$	$H-D\cdots A$
N1—H1A$\cdots$O21^{i}	2.936 (3)	28 (3)
N1—H1B$\cdots$O36^{ii}	2.726 (4)	27 (3)
N1—H1B$\cdots$O32^{ii}	3.066 (4)	28 (3)
N1—H1C$\cdots$O2^{iii}	2.799 (4)	4 (3)
N6—H6$\cdots$O25^{iv}	2.969 (4)	9
N8—H8A$\cdots$O12^{v}	2.906 (5)	34
N8—H8B$\cdots$O35^{vi}	2.900 (4)	5
N9—H9A$\cdots$O36^{vi}	2.794 (4)	7
N9—H9B$\cdots$O25^{iv}	3.384 (4)	30
O22—H22$\cdots$O1^{vii}	2.563 (3)	8 (4)
N11—H11A$\cdots$O26^{iii}	3.082 (4)	10 (4)
N11—H11B$\cdots$O26^{iv}	2.871 (4)	13 (3)
N11—H11C$\cdots$O31^{iv}	2.902 (3)	14 (3)
N16—H16$\cdots$O35^{viii}	2.912 (4)	14
N18—H18A$\cdots$O2^{vii}	2.969 (5)	21
N18—H18B$\cdots$O25^{vii}	2.944 (4)	8
N19—H19A$\cdots$O35^{viii}	3.315 (3)	30
N19—H19B$\cdots$O26^{vii}	2.901 (4)	12
O32—H32$\cdots$O11^{ix}	2.511 (1)	7 (3)

Symmetry codes: (i) $x, y - 1, z$; (ii) $x, y, z + 1$; (iii) $x + 1, y, z$; (iv) x, y, z; (v) $x - 1, y, z + 1$; (vi) $x - 1, y + 1, z + 1$; (vii) $x + 1, y + 1, z$; (viii) $x, y + 1, z$; (ix) $x - 1, y, z$.

Table 7. *Composition of the six oxalic acid complexes with basic amino acids*

Amino acid complexed with oxalic acid	A^{+}	A^{2+}	(I)	(II)	W
DL-Arginine	1	—	1	—	—
L-Arginine	2	—	2	—	—
DL-Lysine	1	—	1	—	2
L-Lysine	—	2	2	1	—
DL-Histidine	—	1	2	—	—
L-Histidine	1	—	1	—	—

A^{+}: zwitterionic amino acid; A^{2+}: doubly positively charged amino acid due to a protonated carboxyl group; (I): semi-oxalate ion; (II): doubly charged oxalate ion; W: water molecule.

hydrogen bond) in the structure are involved in arginine–semi-oxalate interactions against four out of nine in the DL-arginine complex.

The structure of the L-arginine complex contains two sets of crystallographically independent molecules. One set is related to the other by an approximate non-crystallographic **n** glide perpendicular to **a**. This symmetry is only very approximate, particularly in the case of arginine molecules, as all of them are of the L-type and the two sets have somewhat different conformations.

4. A comparative study of amino acid–oxalic acid complexes

The present study completes the X-ray analysis of the complexes of oxalic acid with the L isomers and the DL mixtures of all three basic amino acids, and it is of obvious interest to compare the six crystal structures.

4.1. *Ionization state and stoichiometry*

The compositions of the six complexes, in terms of the ionic species and their stoichiometry, are given in Table 7. The two arginine complexes and the L-histidine complex present a simple picture, with each structure containing singly positively charged zwitterionic amino acid molecules and singly negatively charged semi-oxalate ions in equal proportions. The same situation exists in the DL-lysine complex as well, except for the additional presence of two water molecules. The L-lysine and the DL-histidine complexes present perhaps the only instances where the α-carboxyl group is neutral and protonated in crystal structures containing basic amino acids. Neutral α-carboxyl groups are rare amongst known amino acid structures, one example being in a crystal form of aspartic acid grown in the presence of ornithine and acetic acid (Suresh & Vijayan, 1983). In the DL-histidine complex the O atom *trans* to the α-amino group is protonated. Charge compensation is achieved by a 1:2 stoichiometry of the doubly charged amino acid molecules and the singly charged semi-oxalate ions. The situation is still more

actions among the semi-oxalate ions in the structure. Each is entirely surrounded by arginine molecules such that the complex can be described as an inclusion compound. Such inclusion phenomena have been observed previously in other amino acid complexes, those involving succinic acid providing good examples (Prasad & Vijayan, 1993). The major arginine–semi-oxalate interactions in the complex involve guanidyl and carboxylate groups of semi-oxalate ions. They consist of two sets of type A specific interactions, each involving two almost parallel hydrogen bonds, and two sets of type D specific interactions, each involving two convergent hydrogen bonds (Salunke & Vijayan, 1981; Vijayan, 1988). The carboxyl group of each semi-oxalate ion interacts with the main-chain atoms of two neighbouring arginine molecules through N—H$\cdots$O and O—H$\cdots$O hydrogen bonds. Remarkably, 15 out of the 18 hydrogen bonds (including one bifurcated

complex in the L-lysine complex. O2 is protonated in one of the two crystallographically independent lysine molecules, while O1 is protonated in the other. The four compensating negative charges are provided by two semi-oxalate ions and one doubly charged oxalate ion. Thus, different ionization states of the same molecule can exist in a crystal. Furthermore, they could change when the chirality of half the amino acid molecules are reversed, as occurs when changing from an L complex to a DL complex. Thus, the complexes further confirm the profound effects aggregation and chirality could have on ionization state and stoichiometry.

4.2. Oxalic acid conformation

The six complexes contain nine crystallographically independent semi-oxalate ions and an oxalate ion among them. The structure of free oxalic acid is also available (Delaplane & Ibers, 1969). The conformation of the ion/molecule is determined essentially by the torsion angle about the C—C bond that connects the two carboxyl/carboxylate groups. As illustrated in Fig. 4, this angle varies between 0 and 95°, all except one value lying in the range 0–35°. Thus, the molecule/ion has a propensity to be planar, although large variations from planarity are permitted. In the carboxyl groups H—O—C—O angle is always close to 0°, corresponding to the *syn* conformation.

4.3. Molecular aggregation

The unusual ionization states of the amino acid molecules in the DL-histidine and L-lysine complexes are reflected in their aggregation in two structures. The patterns are very different from those observed so far in other related structures. In the remaining complexes the amino acid molecules aggregate into layers, as usual in this type of crystal structure.

In L-histidine semi-oxalate the amino acid molecules form columns around 2_1 screw axes, stabilized by hydrogen bonds between screw-related molecules involving amino and carboxylate groups, and between translationally related molecules involving imidazole and carboxylate groups. This arrangement is similar to that observed in the complex between L-histidine and L-aspartic acid (Bhat & Vijayan, 1978; Suresh & Vijayan, 1987). More remarkably, the crystal structure of L-histidine semi-oxalate bears a close resemblance to that of DL-histidine glycolate (Suresh & Vijayan, 1996). The aggregation of amino acids in the DL-lysine complex, based on ribbons formed by centrosymmetric dimers, stabilized by two hydrogen bonds between the α-amino and α-carboxylate groups, is similar to those found in several crystal structures of DL-amino acids and their complexes (Soman & Vijayan, 1989), including those of DL-lysine with succinic acid (Prasad & Vijayan, 1991), acetic acid (Soman *et al.*, 1989) and formic acid (Suresh & Vijayan, 1995). As indicated previously, columns in DL-arginine semi-oxalate based on dimers stabilized by guanidyl–carboxylate interactions have been observed in the succinic acid complexes of DL-arginine and, in a poorly defined form, L-arginine (Prasad & Vijayan, 1990). The aggregation pattern of amino acids in L-arginine semi-oxalate is novel.

The semi-oxalate ions form hydrogen-bonded strings in the oxalic acid complexes of DL- and L-histidine, DL-lysine and DL-arginine. One of them is generated by a glide plane, another by a 2_1 screw and the rest by translations (Fig. 5). However, all have a spacing of
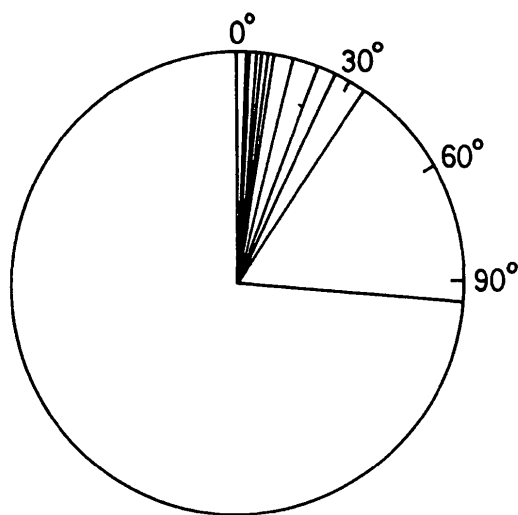

Fig. 4. Distribution of the torsion angles that define the conformation of oxalate/semi-oxalate ion/oxalic acid in various crystal structures.
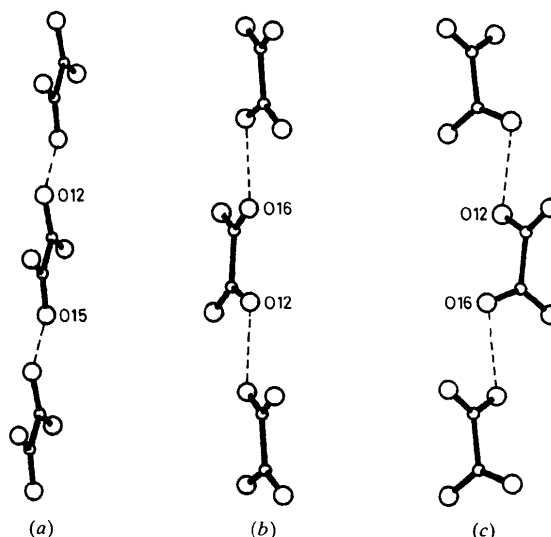

Fig. 5. Examples of semi-oxalate ions forming hydrogen-bonded strings generated by (a) translation as in DL-lysine semi-oxalate, (b) a 2_1 screw as in DL-histidine semi-oxalate and (c) a glide plane as in the DL-arginine semi-oxalate complex.

~5.5 Å between two ions along the string. In the L-arginine complex the semi-oxalate ion is entirely surrounded by arginine molecules, as in inclusion phenomena. In the L-lysine complex two semi-oxalate ions and an oxalate ion form a linear hydrogen-bonded trimer, which then interacts with the surrounding lysine molecules.

Interestingly, the aggregation patterns in the six complexes do not bear any particular resemblance to one another. However, the aggregation of a particular amino acid in its oxalic acid complex tends to have similarities with its aggregation in other structures. The unusual aggregation patterns observed in the DL-histidine and the L-lysine complexes emphasize the importance of the effect of molecular properties, in this case the ionization state, on aggregation. It is also of interest to note that the semi-oxalate ions aggregate into similar strings in four of the six complexes, despite the differences in amino acid partners. Thus, the intrinsic aggregation properties of individual molecules tend to be retained in the complexes, although they are strongly modulated by the presence of other molecules.

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