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A triclinic polymorph of L-argininium chloride

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Key indicators

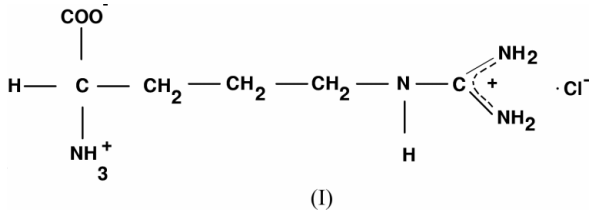
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.042
wR factor = 0.136
Data-to-parameter ratio = 28.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_6H_{15}N_4O_2^+\cdot Cl^-$, crystallizes in the triclinic system with two crystallographically independent argininium residues and two chloride ions in the $P1$ unit cell. In an earlier study, the structure of L-arginine chloride [Mazumdar *et al.* (1969). *Z. Kristallogr.* **130**, 328–339] was determined in the monoclinic space group $P2_1$. In our work, the side-chain conformation has an all-*trans* form in one of the residues, whereas in the other residue, it is in the *gauche* I-*trans-trans-trans* form. All the N atoms, carboxylate groups and chloride ions are involved in a hydrogen-bonding network.

Comment

L-Arginine is an important amino acid present in biological substances. Its guanidyl group is also very important in biological processes (Aoki *et al.*, 1971). L-Arginine phosphate monohydrate is well known for its non-linear optical properties (Jiang *et al.*, 1983). The crystal structures of L-arginine dihydrate (Karle & Karle, 1964), L-arginine hydrochloride monohydrate (Dow *et al.*, 1970), L-arginine phosphate monohydrate (Aoki *et al.*, 1971), L-arginine diarsenate (Zalkin *et al.*, 1989), L-arginine perchlorate (Monaco *et al.*, 1987; Srinivasan & Rajaram, 1997) and L-argininium dinitrate (Ramaswamy *et al.*, 2001) have been reported. In this paper, we report the structure of a triclinic polymorph of L-argininium chloride, (I). An earlier structure determination of (I) was carried out by visual methods in the monoclinic space group $P2_1$ (Mazumdar *et al.*, 1969). The transformation ($10\bar{2}/\bar{1}00/010$) of the present data to the monoclinic setting using the *LEPAGE* routine in *PLATON* (Spek, 1999) resulted in a high R_{int} (0.37) value. In addition, no higher symmetry is detected in our data.



(I)

The unit cell contains two crystallographically independent argininium residues (1 and 2) and two chloride ions (Fig. 1). The equality of the C—O distances in both residues [1.263 (2)/1.248 (2) and 1.254 (2)/1.256 (2) Å] and also the O—C—C bond angles [116.6 (1)/117.4 (1) and 118.7 (1)/115.6 (1)°] indicates symmetric deprotonated carboxylate groups. Furthermore, the guanidyl group is protonated and forms a guanidinium ion. The N—C—N—C torsion angles indicate the

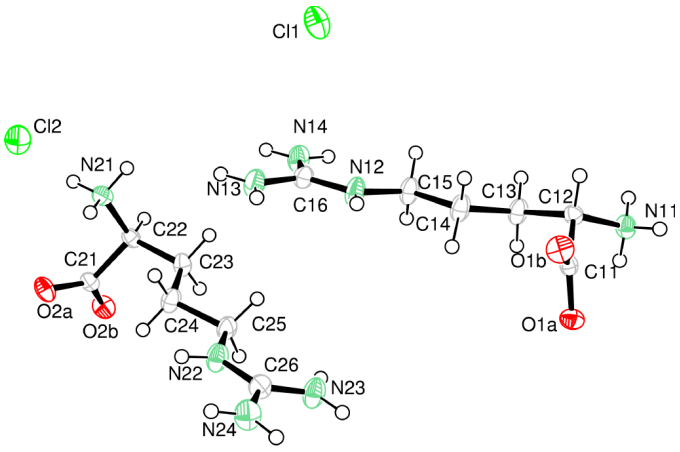


Figure 1
The structure of the title compound, with the atom-numbering scheme and 50% probability displacement ellipsoids (Johnson, 1976).

planarity of the guanidyl group. The conformation angle ψ^1 is −48.5 (2) and −20.2 (2)° for residues 1 and 2, respectively. The deviations of the N^{α} atom from the carboxyl plane are 1.028 (2) and 0.488 (3) Å in 1 and 2, respectively. This tendency for the C—N bond to twist is found in various amino acids (Lakshminarayanan *et al.*, 1967). The side-chain conformation angle χ^1 is *trans* [172.1 (1)°] for residue 1 and *gauche* I [62.3 (2)°] for residue 2, compared to the *trans* conformation in the monoclinic form (Mazumdar *et al.*, 1969). In the present structure, residue 2 has a less favourable *gauche* I conformation. The other three conformation angles χ^2–χ^4 have a *trans-trans-trans* form for both residues.

The α-amino N (N11) and the η-guanidyl N (N13 and N14) atoms of residue 1 are involved in N—H···O hydrogen bonds with carboxylate ions of the translationally related residues 1. Similarly, the α-amino N (N21) and η-guanidyl N (N23 and N24) atoms of residue 2 also form N—H···O hydrogen bonds with the carboxylate ions of the symmetry-related residues 2 (Table 2). In the monoclinic polymorph, the η-guanidyl N atoms are hydrogen bonded with carboxylate ions of the crystallographically independent residues. Interestingly, both structures contain S2 head-to-tail sequences (Vijayan, 1988). The $N^{\eta 2}$ of residue 1 is engaged in a three-centered hydrogen bond with the carboxylate ion (Jeffrey & Saenger, 1991). Residues 1 and 2 individually form two-dimensional molecular networks through intermolecular N—H···O hydrogen bonds. The networks of 1 and 2 are alternately stacked along the *b* cell direction and are linked together by intermolecular N—H···O and N—H···Cl hydrogen bonds (Fig. 2).

Experimental

The title compound was crystallized by slow evaporation from an aqueous solution of a 1:1 stoichiometric ratio of L-arginine and hydrochloric acid.

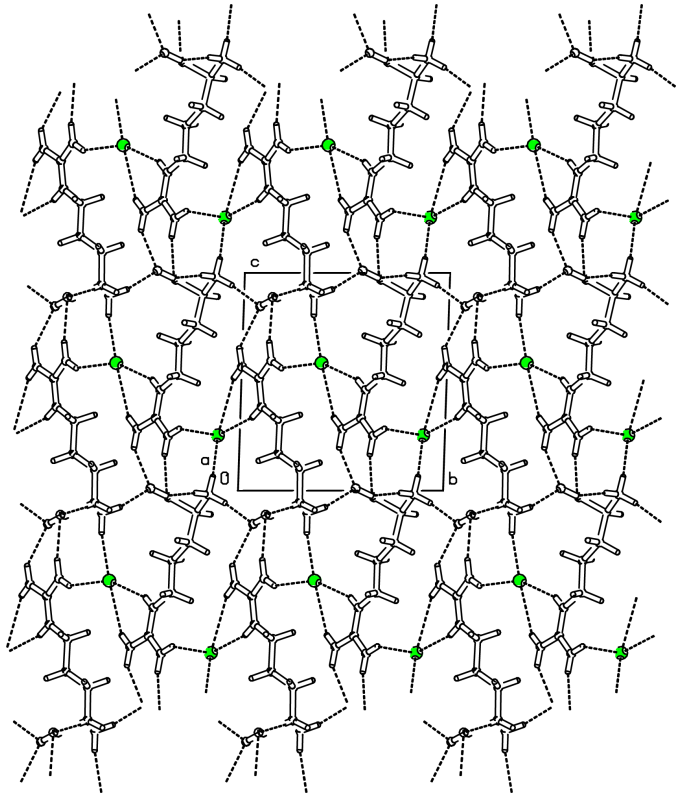


Figure 2
Packing of the molecules, viewed down the *a* axis.

Crystal data

$C_6H_{15}N_4O_2^+\cdot Cl^-$
M_r = 210.67
Triclinic, *P*1
a = 5.1263 (8) Å
b = 9.461 (1) Å
c = 10.322 (2) Å
α = 88.138 (5)°
β = 76.447 (4)°
γ = 89.745 (5)°
V = 486.37 (13) Å^3
Z = 2
D_x = 1.438 Mg m^{-3}
D_m = 1.435 Mg m^{-3}
D_m measured by flotation in carbon tetrachloride and xylene
Mo *Kα* radiation
Cell parameters from 9359 reflections
θ = 2.4–35.3°
μ = 0.37 mm^{-1}
T = 293 (2) K
Block, colorless
0.8 × 0.5 × 0.5 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.74, T_{max} = 0.83
10067 measured reflections
6750 independent reflections
6192 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 35.9°
h = −8 → 8
k = −15 → 15
l = −16 → 16

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.136
S = 1.04
6750 reflections
235 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.48 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}
Absolute structure: Flack (1983), 2179 Friedel pairs
Flack parameter = 0.12 (4)

Table 1
Selected geometric parameters (Å, °).

O1*A*—C11	1.2631 (18)	O2*A*—C21	1.2536 (18)
O1*B*—C11	1.2477 (18)	O2*B*—C21	1.2555 (19)
C12—N11	1.4932 (19)	C22—N21	1.492 (2)
N12—C16	1.315 (2)	C25—N22	1.457 (2)
N12—C15	1.454 (2)	N22—C26	1.319 (2)
C16—N14	1.332 (2)	C26—N23	1.316 (2)
C16—N13	1.343 (2)	C26—N24	1.349 (2)
O1*B*—C11—C12	117.37 (13)	O2*A*—C21—C22	118.67 (13)
O1*A*—C11—C12	116.57 (12)	O2*B*—C21—C22	115.55 (13)
O1*A*—C11—C12—N11	−48.54 (16)	O2*A*—C21—C22—N21	−20.19 (18)
N11—C12—C13—C14	172.10 (14)	N21—C22—C23—C24	62.31 (18)
C12—C13—C14—C15	166.95 (15)	C22—C23—C24—C25	177.49 (14)
C16—N12—C15—C14	176.27 (18)	C23—C24—C25—N22	171.95 (15)
C13—C14—C15—N12	176.72 (16)	C24—C25—N22—C26	−178.56 (17)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N11—H11*A*···Cl1^{i}	0.89	2.35	3.213 (2)	164
N11—H11*B*···O2*A*^{ii}	0.89	2.05	2.907 (2)	161
N11—H11*C*···O1*B*^{iii}	0.89	2.05	2.932 (2)	172
N12—H12*A*···Cl2^{iv}	0.86	2.35	3.166 (2)	159
N13—H13*C*···Cl2^{iv}	0.86	2.66	3.401 (2)	146
N13—H13*D*···O1*A*^{v}	0.86	2.04	2.805 (2)	148
N14—H14*C*···Cl1^{iii}	0.86	2.47	3.240 (2)	150
N14—H14*D*···O1*B*^{vi}	0.86	2.18	2.942 (2)	147
N21—H21*A*···Cl2	0.89	2.28	3.145 (2)	166
N21—H21*B*···O1*A*^{v}	0.89	2.04	2.876 (2)	156
N21—H21*C*···O2*B*^{vii}	0.89	2.04	2.835 (2)	148
N22—H22*A*···Cl1^{viii}	0.86	2.33	3.171 (2)	164
N23—H23*C*···Cl2^{i}	0.86	2.43	3.193 (2)	149
N23—H23*D*···O2*B*^{iv}	0.86	2.10	2.953 (2)	170
N24—H24*C*···O2*A*^{iv}	0.86	2.22	2.963 (2)	144
N24—H24*D*···Cl1^{viii}	0.86	2.78	3.499 (2)	142

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

All H atoms were placed in geometrically calculated positions and included in the refinement in a riding-model approximation, with U_{iso} values equal to $1.2U_{eq}$ of the carrier atom.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL*97.

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