Chain C(5), C(8), C₂¹(4) and C₁²(4) Motifs in DL-Histidinium Perchlorate

S. Asath BAHADUR[†] and S. ATHIMOOLAM

Department of Physics, Kalasalingam University, Anand Nagar, Krishnankoil-626190, Tamil Nadu, India

The title compound, DL-histidinium perchlorate, (C₅H₁₀N₃O₂)⁺·ClO₄⁻, crystallizes in the orthorhombic space group, *Pbca*, with *a* = 9.5281(6) Å, *b* = 9.7227(9) Å, *c* = 20.5794(12) Å and *Z* = 8. The asymmetric part of the unit cell contains a diprotonated monovalent histidinium cation and a perchlorate anion. The amino N atom deviates from the plane of the carboxylate group. Two parallel and opposite chain C(5) motifs run along the *b*-axis of the unit cell, generated through N-H...O hydrogen bonds. It consists of another chain C₂¹(4) motif. Anions contribute to an extensive three-dimensional hydrogen bonding network, leading to the chain C(8) and C₁²(4) motifs. These chain motifs make parallel molecular aggregations along *z* = 1/4 and 3/4.

(Received April 10, 2008; Accepted October 31, 2008; Published on web February 10, 2009)

Proton transfer is one of the most elementary concepts in physics, chemistry and biochemistry, as it is a key process in many important reactions, such as auto ionization in water, acid base neutralization reactions, proton pumping through membrane protein channels and enzyme catalysis. Proton transfer in molecular associations between carboxylic acid and Lewis base confers considerable stability upon the structure making process, generally resulting in more hydrogen-bonding associations, particularly in systems involving protonated amine functional groups. Owing to the relatively low energy of formation, hydrogen bonds can be broken and formed at room temperature, or transformed in other manners, even at very low temperatures. These low-energy characteristics are of vital importance for living functions, and also for nano- and molecular-scale devices.

Histidine, an interesting and essential amino acid, must be present in the diet. It is the only amino acid that has the

imidazole moiety, and acts as a proton donor, a proton acceptor and a nucleophilic reagent. The free base histidine acts as a catalyst for the degradation of various esters.¹ Similarly, polypeptides histidine has been used in the mechanism of a number of enzymes.² In histidine-acid complexes, N-H...O hydrogen bonds are of interest because of their wide-spread biological occurrence. In phosphate salts of histidine, the hydrogen bonds between phosphate groups and histidyl imidazolyl groups are involved in the active-site substrate-binding mechanism of ribonuclease,³ and it are involved in regulating the oxygen affinity of deoxyhemoglobin. Hence, we are in the process of developing new types of proton-transfer compounds and hydrogen-bonding systems. Already, many amino acid-inorganic/organic acid complexes have been reported by the authors. Here, we report on the preparation and X-ray crystal structure of a proton-transfer crystalline complex,

Fig. 1 Perspective view of the molecule, showing thermal ellipsoids at the 50% probability level.

[†] To whom correspondence should be addressed.
E-mail: s_a_bahadur@yahoo.co.in

Table 1 Crystal and experimental data

Empirical formula	(C ₅ H ₁₀ N ₃ O ₂) ⁺ ·(ClO ₄) ⁻
Formula weight	255.62
Temperature	293(2) K
Wavelength	0.71069 Å
Crystal system, space group	orthorhombic, <i>Pbca</i>
Unit cell dimensions	<i>a</i> = 9.5281(6) Å <i>b</i> = 9.7227(9) Å <i>c</i> = 20.5794(12) Å
Volume	1906.5(2) Å ³
<i>Z</i> , Calculated density (<i>D</i> _x)	8, 1.781 Mg/m ³
Absorption coefficient	0.423 mm ⁻¹
<i>F</i> (0 0 0)	1056
2θ _{max}	46°
Reflections collected	1031
Completeness to theta	77.9%
Goodness-of-fit on <i>F</i> ²	1.134
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0439, <i>wR</i> 2 = 0.1158
Largest diff. peak [(Δ <i>σ</i>) _{max}] and hole [(Δ <i>σ</i>) _{min}]	0.369 and -0.211 e.Å ⁻³
Refinement method	full-matrix least-squares on <i>F</i> ²
CCDC No.	682615

Fig. 2 Head-to-tail chain C(5) motif running along the *b*-axis of the unit cell in the opposite direction. H-bonds are shown as dashed lines.

DL-histidinium perchlorate.

DL-Histidinium perchlorate crystals were crystallized in an aqueous solution from a 1:1 stoichiometric ratio of DL-histidine and perchloric acid. Colorless, thin, transparent, plate-shaped crystals were formed within one week. Precise unit-cell dimensions were determined by a least-squares refinement of 25 strong reflections in the range $12^\circ \leq \theta \leq 16^\circ$. Also, the intensities of *hkl* reflections were collected using a CAD-4 X-ray diffractometer. The crystallographic data and details of intensity data collection are given in Table 1.

Generally, in histidine-acid complexes, the histidine molecule exists in two different protonated forms, *viz.*, monoprotonated and diprotonated histidinium cations. In the diprotonated cationic form, both the amino and imidazole rings are protonated, while in the monoprotonated form, one of the sites becomes protonated. In the title compound, the asymmetric unit contains a diprotonated monovalent histidinium cation and a perchlorate anion (Fig. 1). The imidazole ring and the amino groups were protonated with the deprotonated carboxyl group (COO⁻), leading to monovalency for the cation. The deviation of the amine N atom from the carboxylate plane is 0.451(6) Å, and the dihedral angles between the imidazolium ring and carboxylate plane is 52.9(2)°. The back-bone conformation angles ψ^1 and ψ^2 are *cis* and *trans* conformations. The side-chain conformation angles, χ^1 [$-71.3(4)^\circ$], is in a *gauche-II* form, resulting in a closed conformation.⁴ The C^γ atom has a *trans* conformation with respect to the C' atom. The conformations χ^{21} and χ^{22} were observed as $-47.9(5)$ and $137.1(4)^\circ$ for the cation (Table 2), respectively, corresponding to those observed in bis(L-histidinium sulfate)trihydrate.⁵

The anion plays a vital role in hydrogen bonding with the histidinium cations *via* the amine N atom and the N atom of the imidazolium ring. Two separate zigzag (Z1) head-to-tail chains of hydrogen-bonded cations were observed along the *b*-axis *via* the N1-H1B...O1Bⁱⁱⁱ and N1-H1C...O1B^{iv} interactions [symmetry codes: (iii) $-x+1/2, y-1/2, z$; (iv) $-x, y-1/2, -z+3/2$]. In recent days, the hydrogen bonding associations in crystals are denoted with the graph-set motif notation.⁶ Hence, these two head-to-tail interactions can be represented with the chain C(5) motif running along the *b*-axis of the unit cell in the opposite direction. These chain motifs lead to parallel molecular aggregations along $z = 1/4$ and $3/4$ (Fig. 2). This molecular aggregation consists of another chain C₂¹(4) motif between the

Fig. 3 Chain C₂¹(4) motif running along the *a*-axis of the unit cell. H-bonds are shown as dashed lines.

Table 2 Hydrogen bonding geometries (Å, °)

D-H...A	D-H	H...A	D...A	∠D-H...A
N(1)-H(1A)...O(2) ⁱ	0.89	2.3	2.970(4)	132
N(1)-H(1A)...O(3) ⁱⁱ	0.89	2.42	3.142(4)	138
N(1)-H(1B)...O(1B) ⁱⁱⁱ	0.89	1.99	2.847(4)	162
N(1)-H(1C)...O(1B) ^{iv}	0.89	1.89	2.774(4)	175
N(2)-H(2N)...O(5) ^v	0.86	2.55	3.115(5)	124

Symmetry codes: (i) $x-1/2, y, -z+3/2$ (ii) $-x+1, y-1/2, -z+3/2$ (iii) $-x+1/2, y-1/2, z$ (iv) $-x, y-1/2, -z+3/2$ (v) $-x+3/2, y-1/2, z$.

amine and the carboxyl group (Fig. 3). Further, these molecular ensembles are stabilized through bifurcated N-H...O hydrogen bonds between the amine N atom and the perchlorate anion, making the chain C₂²(4) motif. Also, the imidazolium ring makes two linear N-H...O hydrogen bonds with the adjacent anions, leading to a chain C(8) motif.

Acknowledgements

SAB and SA sincerely thank the Vice-Chancellor and Management of the Kalasalingam University, Anand Nagar, Krishnankoil-626 190, for their support and encouragement.

References

1. D. L. Rohling, and S. W. Fox, *Arch. Biochem. Biophys.*, **1967**, *118*, 122.
2. D. H. Meadows, G. C. K. Roberts, and O. Jardetsky, *J. Mol. Biol.*, **1969**, *45*, 491.
3. M. F. Richards, H. W. Wyckoff, W. D. Carlson, N. M. Allewell, M. Lee, and Y. Mitsui, *Cold Spring Harbor Sym. Quant. Biol.*, **1972**, *36*, 25.
4. J. V. Pratap, R. Ravishankar, and M. Vijayan, *Acta Cryst.*, **2000**, *B56*, 690.
5. N. Srinivasan, B. Sridhar, and R. K. Rajaram, *Acta Cryst.*, **2001**, *E57*, o607.
6. J. Bernstein, R. E. Davis, L. Shimoni, and N.-L. Chang, *Angew. Chem. Int. Ed. Engl.*, **1995**, *34*, 1555.