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Two Independent Hydrogen Bonded Complexes of Bis(1-piperidiniumacetate) Hydrochloride in the Crystal and in the PM3 Optimized Structure[*]

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Bis(1-piperidiniumacetate) hydrochloride, $(PAA)_2H^+\cdot Cl^-$, has been synthesized and its structure solved by X-ray diffraction. The crystals belong to the triclinic system with two symmetrically independent hydrogen bonded complexes, denoted A and B, at two different inversion centers. The compound crystallizes in the space group $P\overline{1}$ with $a = 8.559(1)$, $b = 9.625(1)$, $c = 11.441(1)$ Å, $\alpha = 74.85(1)°$, $\beta = 68.22(1)°$, $\gamma = 84.10(1)°$, Z = 2, $R = 0.036$. Each complex consists of two 1-piperidiniumacetate moieties. Four 1-piperidiniumacetates, as zwitterions, are held together by a network of hydrogen bonds of the types O···H···O (2.462(3) and 2.463(3) Å), N–H···O (2.755(2) Å) and N–H···Cl (3.167(2)Å). Both N-H atoms in complex A interact with chlorine anions. A number of week C–H···Cl contacts stabilize the three-dimensional crystal structure. In the isolated molecule of $(PAA)_2H^+\cdot Cl^-$ optimized by the PM3 method, there also are two independent hydrogen bonded complexes. In complex A the neutral form of 1-piperidineacetic acid interacts with its anionic form, while in complex B the 1-piperidiniumacetic acid, as a cation, forms a hydrogen bond with its zwitterionic form. FTIR spectrum of bis(1-piperidiniumacetate) hydrochloride has been analyzed and discussed.

Key words: 1-piperidineacetic acid, hydrogen bond, X-ray diffraction, FTIR and NMR spectroscopy, PM3 calculations

Amino acids and peptides constitute one of the most widely studied classes of chemical compounds. Glycine and its methylated analogues form complexes with mineral acids exhibiting interesting physical properties like ferroelastic, ferroelectric or antiferroelectric behavior often associated with transitions to commensurate or incommensurate phases [1–7]. According to the structural analysis of ferroelectric triglycine sulfate [8] there are two kinds of glycine groups, glycinium ions and zwitterions. Such configurations of glycine ions interconnected by short O–H···O hydrogen bonds are regarded as particularly important for the ferroelectric behavior of this crystals. In the ferroelectric and paraelectric structure of $(Glycine)_2HNO_3$, one of the glycine molecules has the zwitterion configuration and the other is monoprotonated [9,10]. A similar structure has been found in diglycine hydrochloride [11], hydrobromide [12], hydroiodide [13] and disarcosine hydrobromide [14]. In all

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[*] Dedicated to Prof. M. Szafran on the occasion of his 70th birthday.
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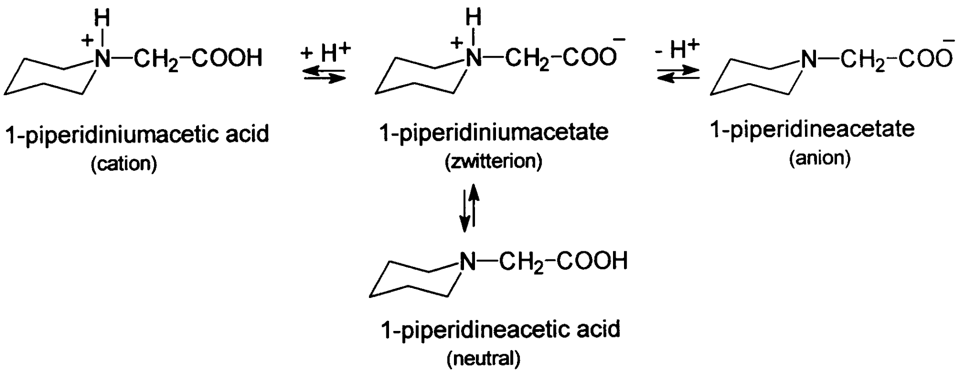
above mentioned structures the molecules are held together by a network of N–H···X, N–H···O and O–H···O hydrogen bonds.

We are presently engaged in a systematic studies of the structural and spectroscopic properties of 1-piperidineacetic acid and its complexes with mineral acids [15–19]. 1-Piperidineacetic acid (PAA) can be treated as a glycine analogue, in which an amino group is involved in an alicyclic ring. The PAA molecule has an amphoteric character and can exist in an anionic or a cationic form, as well as in the two uncharged tautomeric forms, one of which, with the neutral amino group and carboxylate acid group, the other in the dipolar zwitterionic form (Scheme 1). When the molecule acts as an acid, an H atom is released from the former group, forming an anion, while a cation is formed when the molecule acts as a base by accepting a proton at the negatively charged carboxylate group of the zwitterion. PAA exists as a zwitterion both in the crystalline state, in solution and in the gas phase [15,19]. Recently, we have studied the structure of the 2:1 complex of 1-piperidineacetic acid with $HClO_4$, $(PAA)_2H^+ \cdot ClO_4^-$, in which two zwitterions of the 1-piperidiniumacetate are held by a short and symmetrical O···H···O hydrogen bond forming a homoconjucated cation, further incorporated by intermolecular N–H···O interactions in a network of hydrogen bonds [18].

Scheme 1



The main difference between the structures of $(PAA)_2H^+ \cdot ClO_4^-$ and $(Glycine)_2H^+ \cdot X^-$ is that the former has a bulkier side-chain on the α-carbon and hence its zwitterion is more polarizable than that of glycine. It is known that large polarizable ions are more stable than smaller less polarizable ions [20]. The effect of the bulky perchlorate anion cannot be neglected. To solve this problem, in the present study we prepared 2:1 complex of 1-piperidineacetic acid with hydrochloride. The structure of $(PAA)_2H^+ \cdot Cl^-$ is solved by the X-ray diffraction method and the complex is studied by FTIR spectroscopy. The crystal structure of $(PAA)_2H^+ \cdot Cl^-$ is compared with that of the isolated molecule simulated using the PM3 method.

EXPERIMENTAL

1-Piperidineacetic acid (PAA·H_2O) was prepared by neutralization of 1-piperidiniumacetic acid chloride (10 g) [19] with K_2CO_3 (3.88 g) in water (100 cm^3). After evaporation to dryness, the mixture of 1-piperidineacetic acid and KCl was extracted by chloroform in a Soxhlet apparatus for 50 hrs. The solvent was then evaporated to dryness and crude 1-piperidineacetic acid monohydrate was crystallized from the acetonitrile-methanol mixture (5:1) m.p. 204–206°C; m.p. 202–206°C from ref. [21], 7.44 g, 93% of yield.

Bis(1-piperidiniumacetate) hydrochloride was obtained by mixing stoichiometric amounts of 1-piperidineacetic acid with 1-piperidiniumacetic acid chloride [19] in methanol solution and followed by solvent evaporation to dryness under reduced pressure. The crude product was crystallized from acetonitrile, m.p. 178–180°C. Analysis of $C_{14}H_{27}N_2O_4Cl$: calculated: 52.09 %C, 8.43 %H, 8.68 %N; found: 51.82 %C, 8.56 %H, 8.61 %N. The purity of the compound was checked by ^1H and ^{13}C NMR. ^1H (ppm, D_2O): 3.01, C(2,6)-H_{ax}; 3.58, C(2,6)-H_{eq}; 1.93, C(3,5)-H_{ax}; 1.84, C(3,5)-H_{eq}; 1.49, C(4)-H_{ax}; 1.75 C(4)-H_{eq}; 3.84, C(7)-H; ^{13}C (ppm, D_2O): 57.04, C(2,6); 25.51 C(3,5); 23.82, C(4); 60.38, C(7); 172.15, C(8). The deuterated complex 2:1 of the 1-piperidineacetic acid with hydrochloride acid was prepared by three-fold exchange with D_2O, followed by removal of excess of D_2O in vacuum. The residue was recrystallized from CH_3OD.

The FTIR spectra were measured on a Bruker IFS 113v instrument. Each spectrum consists of 250 scans at 31°C. Solid state spectra were recorded in Nujol and Fluorolube mulls using KBr plate.

The NMR spectra were recorded on a Varian Gemini 300VT spectrometer operating at 300.07 and 75.46 MHz for ^1H and ^{13}C, respectively. The spectra were measured in D_2O with 3-(trimethylsilyl)-propionic-d_4 acid sodium salt as internal reference. The sample concentration was 0.3 mol·dm^{-3}.

X-ray diffraction: The crystals of bis(1-piperidiniumacetate) hydrochloride were obtained from the acetonitrile solution by slow evaporation. Diffraction measurements were carried out at ambient temperature on KUMA KM-4 diffractometer equipped with CCD detector by MoKα radiation, for the 60 mm distance between the crystal and the detector. Data reduction were carried out using KM4 CCD software [22]. The structure was solved by direct methods using SHELXS-97 program [23] and refined on $F^{2'}$s by full-matrix least-squares methods with SHELXL-97 program [24]. The parameters of non-hydrogen atoms were refined with anisotropic displacement factors. Hydrogen atoms were located on a difference Fourier map and their displacement parameters were refined with isotropic method. The final R-factor equals 0.036 for 2975 independent reflections and 297 refined parameters. Crystal data are given in Table 1 and the final fractional atomic coordinates of atoms in Table 2. The supplementary information in the CIF form are available from Cambridge Crystallographic Data-base Centre, No CCDC 209390.

Table 1. Crystal data and structure refinement for bis(1-piperidiniumacetate) hydrochloride.

Empirical formula	$C_{14}H_{26}N_2O_4$ HCl
Formula weight	322.83
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 8.559(1) Å
	b = 9.625(1) Å
	c = 11.441(1) Å
	α = 74.85(1)°
	β = 68.22(1)°
	γ = 84.10(1)°
Volume	844.8(3) $Å^3$
Z	2
Calculated density	1.269 g/cm^3

Table 1 (continuation)

Absorption coefficient	0.243 mm^{-1}
$F(000)$	348
Crystal size	0.2×0.2×0.35 mm
θ range for data collection	3.08 to 24.99°
widctlpar Index ranges	$-10 \le h \le 10$ $-11 \le k \le 11$ $-10 \le l \le 13$
Reflections collected / unique	6571 / 2975 [R(int) = 0.0325]
Completeness to $\theta = 24.99$	99.6%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2975 / 0 / 297
Goodness-of-fit on F^2	0.974
Final R indices $[I > 2\sigma(I)]$	R1 = 0.0360, wR2 = 0.0919
R indices (all data)	R1 = 0.0551, wR2 = 0.0995
Extinction coefficient	0.023(4)
Largest diff. peak and hole	0.242 and –0.171 e·Å^{-3}

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (Å^2×10^3) for bis(1-piperidiniumacetate) hydrochloride. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor. Symmetry transformation for atomic coordinates of the second half of complex A and B: –x+3, –y+2, –z and –x+2, –y+1, –z, respectively.

Atom	x	y	z	U(eq)
Cl(1)	0.8618(1)	0.7885(1)	0.4976(1)	54(1)
N(1A)	0.9581(2)	1.0633(2)	0.2615(1)	31(1)
C(2A)	0.8363(2)	1.1682(2)	0.3274(2)	44(1)
C(3A)	0.6564(2)	1.1165(2)	0.3770(2)	47(1)
C(4A)	0.6082(3)	1.0852(3)	0.2721(2)	59(1)
C(5A)	0.7317(3)	0.9766(3)	0.2107(2)	60(1)
C(6A)	0.9112(3)	1.0300(3)	0.1577(2)	48(1)
C(7A)	1.1325(2)	1.1213(2)	0.2082(2)	40(1)
C(8A)	1.2643(2)	1.0187(2)	0.1465(2)	36(1)
O(1A)	1.3932(2)	1.0807(1)	0.0549(1)	51(1)
O(2A)	1.2421(2)	0.8900(1)	0.1870(1)	64(1)
H(11A)	0.954(2)	0.983(2)	0.323(2)	43(5)
H(21A)	0.854(2)	1.254(2)	0.262(2)	60(6)
H(22A)	0.877(2)	1.177(2)	0.399(2)	59(6)
H(31A)	0.585(3)	1.191(2)	0.418(2)	63(6)
H(32A)	0.645(2)	1.036(2)	0.442(2)	51(6)
H(41A)	0.606(3)	1.167(3)	0.211(2)	73(8)
H(42A)	0.491(3)	1.049(2)	0.307(2)	71(6)
H(51A)	0.705(3)	0.963(2)	0.142(2)	76(7)
H(52A)	0.725(3)	0.881(3)	0.275(2)	77(7)
H(61A)	0.923(2)	1.115(2)	0.097(2)	47(5)
H(62A)	0.999(2)	0.954(2)	0.124(2)	44(5)
H(71A)	1.133(2)	1.208(2)	0.148(2)	47(5)
H(72A)	1.159(2)	1.141(2)	0.282(2)	65(6)
H(1A)	1.500	1.000	0	131(2)
N(1B)	1.2635(2)	0.5939(2)	0.2473(1)	37(1)
C(2B)	1.2654(3)	0.6015(3)	0.3762(2)	52(1)
C(3B)	1.4321(3)	0.6578(3)	0.3599(3)	66(1)
C(4B)	1.5798(4)	0.5712(3)	0.2930(3)	70(1)
C(5B)	1.5724(3)	0.5586(3)	0.1662(3)	65(1)

Table 2 (continuation)

C(6B)	1.4056(3)	0.4999(3)	0.1864(2)	52(1)
C(7B)	1.0994(2)	0.5451(2)	0.2564(2)	44(1)
C(8B)	1.0914(2)	0.5706(2)	0.1223(2)	45(1)
O(1B)	1.0000(2)	0.4826(2)	0.1105(1)	59(1)
O(2B)	1.1719(2)	0.6682(2)	0.0355(1)	80(1)
H(11B)	1.283(2)	0.680(2)	0.199(2)	49(6)
H(21B)	1.248(2)	0.510(2)	0.424(2)	57(6)
H(22B)	1.171(3)	0.665(2)	0.409(2)	65(6)
H(31B)	1.427(3)	0.658(3)	0.445(3)	94(9)
H(32B)	1.446(3)	0.756(3)	0.307(2)	65(7)
H(41B)	1.578(3)	0.481(3)	0.346(2)	78(8)
H(42B)	1.686(4)	0.609(3)	0.274(3)	94(9)
H(51B)	1.663(3)	0.503(3)	0.128(2)	78(7)
H(52B)	1.591(3)	0.653(3)	0.115(2)	79(8)
H(61B)	1.382(2)	0.404(2)	0.250(2)	63(6)
H(62B)	1.397(3)	0.499(2)	0.109(2)	64(7)
H(71B)	1.089(2)	0.445(2)	0.301(2)	51(5)
H(72B)	1.013(3)	0.599(2)	0.304(2)	55(6)
H(1B)	1.000	0.500	0	123(1)

Computation details: The PM3 [25] semiempirical method was used, as an implement in the AMPAC program package [26]. In all cases, the PRECISE and GRAD keywords were used and the geometry was calculated with SYMMETRY keyword. The X-ray geometry was used as starting input file.

RESULTS AND DISCUSSION

X-ray structure: 1-Piperidineacetic acid forms a crystalline complex with hydrochloride in the stoichiometry 2:1. Fig. 1 shows the atom numbering of two centrosymmetric independent complexes denoted by A and B. Selected bond lengths,

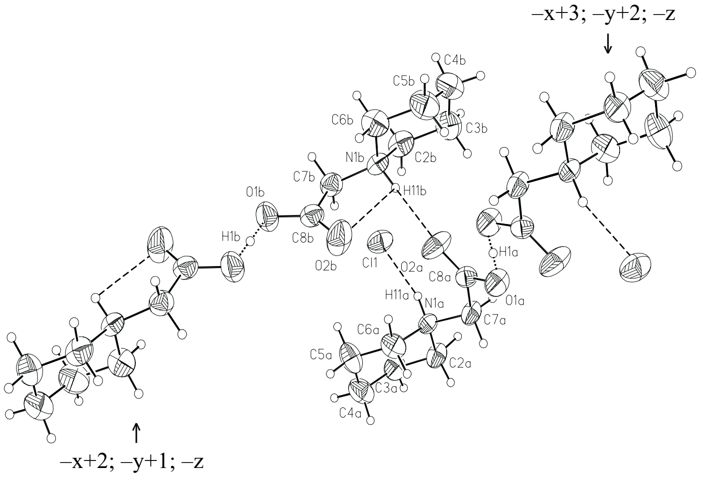


Figure 1. Molecular structure of symmetrical complexes of bis(1-piperidiniumacetate) hydrochloride and atomic numbering showing 50% probability displacement ellipsoids.

bond and torsion angles are given in Table 3. Four 1-piperidiniumacetates, as zwitterions, form two independent homoconjugated complexes, A and B, linked through hydrogen bonds whose hydrogen atoms are at special positions at two different crystallographic inversion center "d" (½,0,0) and "c" (0,½,½), respectively, according to the Wyckoff notation [27] in the triclinic unit cell. Two carboxylate groups are bridged by a hydrogen atom from the hydrochloride, forming homoconjugated complexes with strong, linear and centrosymmetric hydrogen bonds with the O···H···O distances of 2.463(3) and 2.462(3) Å in complexes A and B, respectively.

Table 3. Experimental and calculated bond lengths (Å) bond and torsion angles (deg) for bis(1-piperidiniumacetate) hydrochloride.

	X-ray		PM3			
	Complex A	Complex B	Complex A		Complex B	
Bond lengths	Zwitterion	Zwitterion	Neutral	Anion	Cation	Zwitterion
N(1)–C(2)	1.508(2)	1.502(2)	1.500	1.501	1.523	1.518
C(2)–C(3)	1.517(3)	1.508(3)	1.523	1.524	1.522	1.523
C(3)–C(4)	1.511(3)	1.509(3)	1.520	1.520	1.521	1.520
C(4)–C(5)	1.520(3)	1.511(4)	1.520	1.520	1.521	1.521
C(5)–C(6)	1.517(3)	1.505(3)	1.523	1.523	1.519	1.523
N(1)–C(6)	1.500(2)	1.503(2)	1.503	1.502	1.518	1.517
N(1)–C(7)	1.493(2)	1.485(2)	1.497	1.500	1.519	1.513
C(7)–C(8)	1.514(2)	1.515(3)	1.523	1.533	1.523	1.575
N(1)–H(11)	0.89(2)	0.86(2)	–	–	1.061	1.064
C(8)–O(1)	1.273(2)	1.274(2)	1.341	1.256	1.328	1.237
C(8)–O(2)	1.212(2)	1.217(2)	1.218	1.267	1.256	1.265
O(1)–H(1)	1.232(2)	1.231(2)	0.974	–	0.974	–
Bond angles						
N(1)–C(2)–C(3)	111.1(2)	110.3(2)	110.59	110.28	110.49	110.69
C(2)–C(3)–C(4)	112.7(2)	112.8(2)	110.89	110.94	111.40	111.07
C(3)–C(4)–C(5)	109.2(2)	110.5(2)	110.04	110.23	110.57	110.83
C(4)–C(5)–C(6)	111.3(2)	111.0(2)	111.06	111.01	110.54	111.08
C(6)–N(1)–C(2)	111.7(2)	109.9(2)	111.03	110.89	109.71	110.23
N(1)–C(6)–C(5)	111.3(2)	110.8(2)	110.87	110.45	110.59	110.64
C(7)–N(1)–C(2)	109.6(2)	112.7(2)	112.36	111.78	109.57	112.06
C(7)–N(1)–C(6)	111.3(2)	111.4(2)	110.06	111.80	111.39	112.43
N(1)–C(7)–C(8)	113.0(2)	110.3(2)	111.94	111.64	113.00	105.22
O(1)–C(8)–C(7)	114.0(2)	115.1(2)	114.24	120.43	113.78	120.02
O(2)–C(8)–C(7)	119.7(2)	119.6(2)	126.70	120.95	125.68	113.38
O(2)–C(8)–O(1)	126.2(2)	125.3(2)	119.04	118.62	120.49	126.60
C(8)–O(1)–H(1)	115.4(2)	114.8(2)	113.02	–	113.32	–
Torsion angles						
N(1)–C(2)–C(3)–C(4)	–54.7(3)	–55.3(3)	–57.39	–57.27	–56.44	–56.78
C(2)–C(3)–C(4)–C(5)	56.0(3)	53.2(3)	56.44	55.89	55.46	55.41
C(3)–C(4)–C(5)–C(6)	–56.7(3)	–53.9(3)	–55.90	–55.66	–56.19	–55.45
N(1)–C(6)–C(5)–C(4)	57.1(3)	58.0(3)	56.31	56.84	58.49	56.86
C(2)–N(1)–C(6)–C(5)	–54.9(2)	–59.7(2)	–56.92	–58.15	–59.05	–57.83
C(6)–N(1)–C(2)–C(3)	53.3(2)	57.7(2)	57.41	58.32	57.74	57.82
C(7)–N(1)–C(2)–C(3)	177.2(2)	–177.5(2)	–178.85	–176.20	–179.68	–176.17
C(7)–N(1)–C(6)–C(5)	–177.8(2)	174.7(2)	178.04	176.38	179.46	176.35

Table 3 (continuation)

C(2)–N(1)–C(7)–C(8)	176.9(2)	167.6(2)	61.72	147.03	–175.78	113.37
C(6)–N(1)–C(7)–C(8)	–59.0(2)	–68.4(2)	–174.00	–87.99	–54.20	–121.82
O(2)–C(8)–C(7)–N(1)	–30.5(3)	–28.2(3)	80.95	23.30	24.92	4.04
O(1)–C(8)–C(7)–N(1)	150.6(2)	150.5(2)	–100.73	–155.71	–157.66	–175.71
O(2)–C(8)–O(1)–H(1)	3.6(2)	–1.6(2)	2.70	–	–2.57	–

The two complexes play different roles in crystals. In complex A, both N^+–H atoms interact with chlorine anions by two N(1A)–H(11A)···Cl(1) hydrogen bonds of the length 3.167(2) Å. In complex B, the N^+–H atoms participate only in a bifurcated hydrogen bond, of which one is intramolecular, N(1B)–H(11B)···O(2B) of the length 2.717(2) Å and the other is intermolecular, N(1B)–H(11B)···O(2A) of the length 2.755(2) Å. Complexes A and B are placed nearly perpendicular to each other in the crystals (Fig. 2). The geometry of the hydrogen bonds is given in Table 4. Both complexes A and B form an infinite hydrogen bonded chains parallel to the *y* axis (Fig. 3).

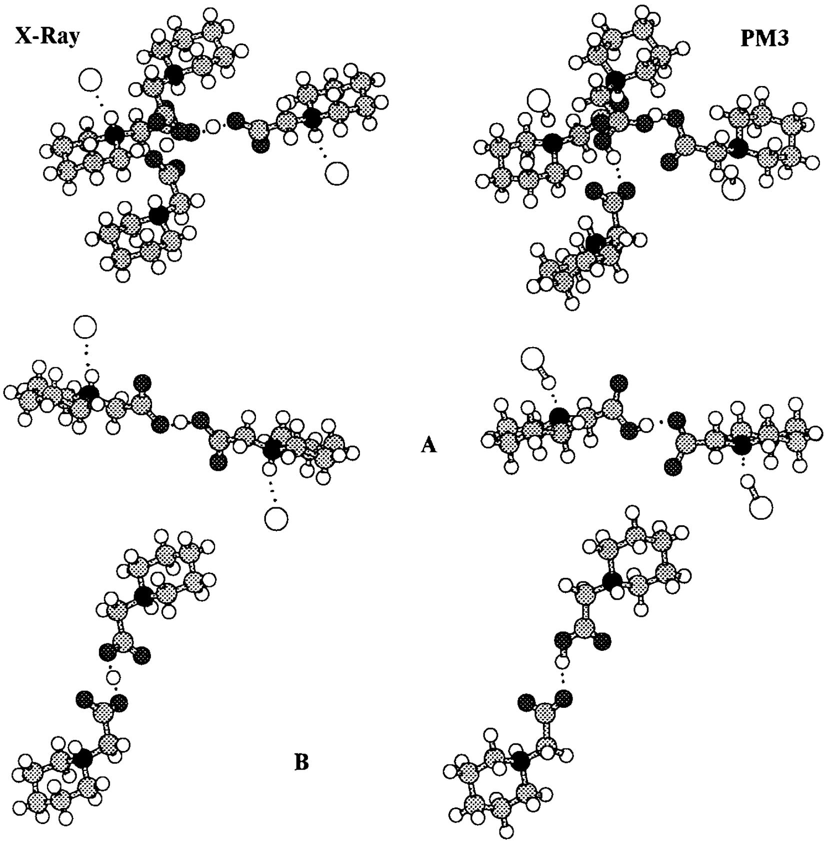


Figure 2. The experimental and calculated structures of the molecules of bis(1-piperidiniumacetate) hydrochloride and separately structures of complexes A and B. Complexes A and B are joined by the N(1B)–H(11B)···O(2A) hydrogen bond.

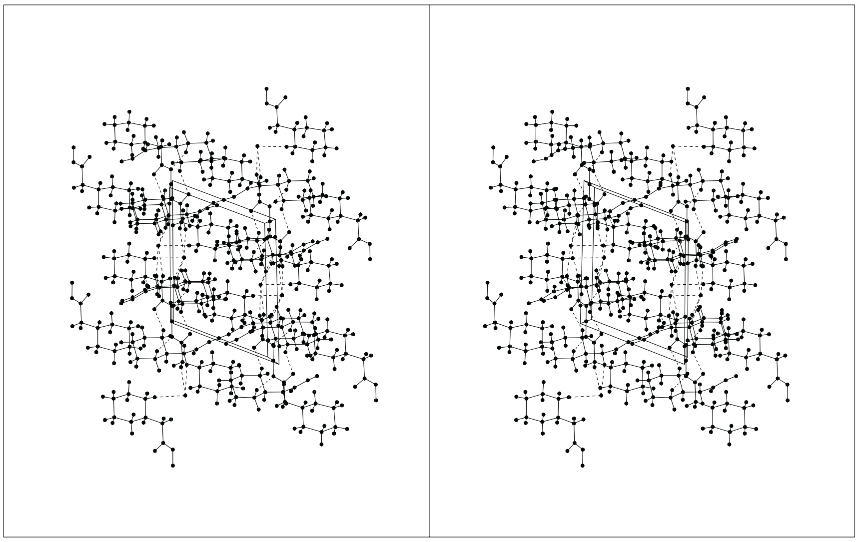


Figure 3. A stereoview of the packing of bis(1-piperidiniumacetate) hydrochloride viewed along the *b* axis with the *a* axis vertical and the *c* axis horizontal. Short symmetrical O···H···O bonds are represented by continuous lines, while N–H···O, N–H···Cl and C–H···O bonds are represented by dashed lines.

Table 4. Experimental and calculated hydrogen-bonds in bis(1-piperidiniumacetate) hydrochloride (Å and deg.).

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
X-ray				
O(1A)–H(1A)···O(1A)[a]	1.232(1)	1.232(1)	2.463(3)	180.0
O(1B)–H(1B)···O(1B)[b]	1.231(1)	1.231(1)	2.462(3)	180.0
N(1B)–H(11B)···O(2B)	0.86(2)	2.427(2)	2.717(2)	100(1)
N(1B)–H(11B)···O(2A)	0.86(2)	1.991(2)	2.755(2)	147(1)
N(1A)–H(11A)···Cl(1)	0.89(2)	2.303(2)	3.167(2)	163(1)
PM3				
O(1A)–H(1A)···O(1A)	0.974	1.737	2.670	168.2
O(1B)–H(1B)···O(1B)	0.974	1.740	2.694	165.8
N(1B)–H(11B)···O(2A)	1.060	1.687	2.642	147.2
Cl–H···N(1A)[c]	1.326	1.737	3.033	163.9
Cl–H···N(1A)[d]	1.370	1.663	3.018	168.4

Symmetry code: [a] –x+3, –y+2, -z; [b] –x+2, –y+1, –z; [c] in the neutral moiety; [d] in the anionic moiety.

In complex B the piperidine rings have a little distorted chair conformation. The asymmetry parameter equals 2.9, while the rings in complex A have better ideal chair conformation, the asymmetry parameter has the value of 1.5 [28]. Larger deformation of the ring in complex B can be a result of the intramolecular hydrogen bond.

A similar bifurcated N^+–H···O hydrogen bond has been found in 1-piperidineacetic acid monohydrate [15], its complex with perchloric acid [16], α-glycine and β-glycine [29]. The CH_2COO groups in both complexes are at the equatorial positions relative to the piperidinium ring.

In complexes A and B, the N(1)–C(7)–C(8)–O(1) moieties have almost *trans* conformation, the torsion angles are 150.6(2)° and 150.5(2)°, respectively. The carboxylic groups have the usual *cis* conformation, the torsion angle of O(2)–C(8)–O(1)–H(1) in complexes A and B are 3.6(2)° and –1.7(2)°, respectively. In both complexes the C(8)–O(1) bond is longer by *ca.* 0.059(2) Å than the C(8)–O(2) one, because O(1) is engaged in stronger hydrogen bond (Table 3). These lengths are not much different from those in $(PAA)_2H^+{\cdot}ClO_4^-$ and in $PAA{\cdot}H_2O$, where they are 1.277(2), 1.231(2) [18] and 1.249(2), 1.242(2) [15], respectively.

A number of weak C–H···Cl contacts combine both complexes with chlorine ion, which stabilizes the three-dimensional crystal structure (Fig. 3, Table 5). Additionally, the structures of the complexes investigated are stabilized by electrostatic interactions between the N^+ atom and O(1) and O(2) atoms (Table 5). These N···O intramolecular distances are similar to those in $PAA{\cdot}H_2O$ [15], $(PAA)_2H^+{\cdot}ClO_4^-$ [18] and betaines [30].

Table 5. Experimental C–H···Cl contacts and calculated N- - - O distances (Å) in bis(1-piperidiniumacetate) hydrochloride.

C(2B)–H···Cl(1)	3.684
C(2B)–H···Cl(1)^a	3.769
C(7A)–H···Cl(1)^b	3.707
C(7B)–H···Cl(1)^a	3.755
C(2A)–H···Cl(1)	3.692
C(3A)–H···Cl(1)	3.652
N(1A) - - - O(2A)	2.791^{c,d} 3.217^e 2.800^f
N(1A) - - - O(1A)	3.588^{c,d} 3.315^e 3.645^f
N(1B) - - - O(2B)	2.718^{c,d} 2.905^g 2.494^d
N(1B) - - - O(1B)	3.560^{c,d} 3.689^g 3.621^d

Symmetry code: ^{a} –x+2; –y+1; –z+1; ^{b} –x+2, –y+2, –z+1; ^{c} from the X-ray data; ^{d} in the zwitterionic moiety; ^{e} in the neutral moiety; ^{f} in the anionic moiety; ^{g} in the cationic moiety.

It is interesting to compare the molecular structure of the complex investigated with these of $(PAA)_2H^+\cdot ClO_4^-$ [18] and $(Glycine)_2H^+\cdot X^-$ [9–13]. Both in $(PAA)_2H^+\cdot Cl^-$ and $(PAA)_2H^+\cdot ClO_4^-$ the 1-piperidineacetic acid moieties exist in the zwitterionic form in the crystals, the difference is between them due to the counter ion effect. However, in glycine derivative crystals one glycine molecule exists as the zwitterion and the other is in the cationic form $[H_3N^+–CH_2–COO^-\cdot HOOC–CH_2–N^+H_3]\ X^-$. The glycine molecules are interconnected by N–H···O, O–H···O and N–H···X hydrogen bonds.

PM3 calculations: The PM3 optimized structure of $(PAA)_2H^+\cdot Cl^-$ is shown in Fig. 2. The calculated bond lengths, bond and torsion angles are given in Table 3. The large dipole moment (18.14 D) suggests a general asymmetry of the conformation of the compound. In the gas phase there are also two complexes A and B, which are nearly perpendicular to each other, similarly as in the crystals (Fig. 2). For the sake of clarity Fig. 2 presents also separately the crystallographic and calculated structures of the complexes A and B. In the structure optimized by the PM3 methods, the 1-piperidineacetic acid appears in all possible forms presented in Scheme 1. As shown in Fig. 2, the main differences between X-ray and PM3 structures are in hydrogen bonds. In the PM3 structures of complexes A and B the O–H···O hydrogen bonds are asymmetric and *ca.* 0.2 Å longer than in the crystal. In the case of complex A the N–H···Cl hydrogen bond in the crystal is replaced by N···HCl in the PM3 structure (Table 4), hence the neutral form of PAA interacts with its anionic form. The difference in N···Cl hydrogen bonds is a consequence of a change in electrostatic Coulombic interactions of Cl atom from intermolecular (with three surrounding molecular interaction in the crystal (Fig. 3)) to the intramolecular interaction in a single molecule, like in the gas phase [31,32]. The intermolecular electrostatic interactions decrease the proton acceptor ability of Cl ion and favor proton transfer. In complex B the cation of PAA and its zwitterion are connected by the asymmetric O–H···O hydrogen bond (Table 4). A similar situation was observed in crystals of diglycine hydrochloride and sarcosine hydrobromide [11,14].

FTIR spectra: The solid state spectrum of bis(1-piperidiniumacetate) hydrochloride and its deuterated analogue is shown in Fig. 4. There are three types of hydrogen bonds in the compound investigated, N–H···O (2.755(2) Å), N–H···Cl (3.167(2) Å) and O···H···O (2.462(3) Å). The N–H stretching vibration band overlaps the C–H stretching bands and appears as a broad band in the 3050–2550 cm^{-1} region, however, two significantly strong bands can be resolved at 3046 and *ca*. 2670 cm^{-1} attributed to the νN–H···Cl and νN–H···O modes, respectively. In the deuterated species these bands are shifted to the 2300–1980 cm^{-1} region. The short and symmetrical O···H···O hydrogen bonds are characterized by a broad and intense absorption with several Evans windows in 1500–400 cm^{-1} region. The centre of gravity, ν_H, [33] of this absorption is at 960 cm^{-1}. The deuteration resulted only in a decrease in the intensity of a broad absorption, ν_D is at 954 cm^{-1}. The isotope ratio $\nu_H/\nu_D \approx 1.0$ confirms the presence of a short hydrogen bond in the compound investigated. A similar broad absorption is present in the spectra of 2:1 complexes of betaines [34–37] and type A acid salts of carboxylic acids [38,39]. The strong absorption at 1737 cm^{-1} is attributed to the νC=O engaged in the hydrogen bond. The deuteration caused a shift of the band to 1690 cm^{-1}. This large difference observed between the νC=O bands is probably caused by its coupling with deformation OH or OD vibrations.

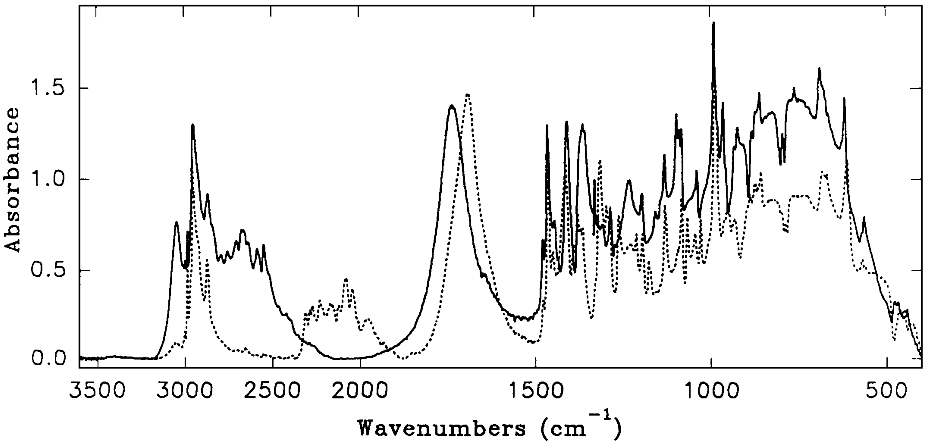


Figure 4. FTIR spectrum of bis(1-piperidiniumacetate) hydrochloride; dotted line after deuteration.

CONCLUSIONS

The molecular and crystal structures of the 2:1 complex of the piperidineacetic acid with HCl have been studied by X-ray diffraction, the PM3 calculations and FTIR spectra. The crystal comprises two homoconjugated complexes A and B joined by the short and symmetrical O···H···O hydrogen bonds of the lengths 2.463(3) and 2.462(3) Å, respectively. In complex A, each N^+–H group interacts with the Cl^- anion; the N–H···Cl distance is 3.167(2) Å. In complex B, the N^+–H group forms a bifurcated hydrogen bond with oxygen atoms, one is intramolecular (N(1B)–H(11B)···O(2B), 2.717(2) Å, and the other is the intermolecular, (N(1B)–H(11B)···O(2A), 2.755(2) Å.

The PM3 calculations also reproduce two complexes A and B, but with longer and asymmetrical hydrogen bonds. In complex A, 1-piperidineacetic acid and 1-piperidineacetate are linked by the O–H···O hydrogen bond. The nitrogen atoms of complex A further interact with HCl *via* the N···H–Cl hydrogen bonds. In complex B, the protonated 1-piperidineacetic acid forms the O–H···O hydrogen bond with the zwitterionic form of 1-piperidineacetic acid.

The FTIR spectrum of the compound investigated confirmed its structure determined by X-ray diffraction method.

REFERENCES

1. Zobetz E. and Preisinger A., *Monatsh. Chem.,* **120**, 291 (1989).
2. Haussühl S., *Z. Kristallogr.,* **188**, 311 (1989).
3. Maeda M., *J. Phys. Soc. Japan,* **57**, 2162 (1988).
4. Jiyang W., Gnanam F.D. and Haussühl S., *Z. Kristallogr.,* **175**, 155 (1986) and references cited therein.
5. Mostad A. and Natarajan S., *Z. Kristallogr.*, **197**, 209 (1991) and references cited therein.
6. Albers J., *Ferroelectrics*, **78**, 3 (1988).
7. Schaack G., *Ferroelectrics*, **104**, 147 (1990) and references cited theein.
8. Hoshino S., Okaya Y. and Pepinsky R., *Phys. Rev.,* **115**, 323 (1959).
9. Sato S., *J. Phys. Soc. Japan.,* **25**, 185 (1968).
10. Baran J., Barnes A.J. and Ratajczak H., *Spectrochim. Acta,* **51A**, 197 (1995).
11. Natarajan S., Muthukrishnan C., Bahadur S.A., Rajaram R.K. and Rajan S.S., *Z. Kristallogr.,* **198**, 265 (1992).
12. Buerger M.J., Barney E. and Hahn T., *Z. Kristallogr.*, **108**, 130 (1956).
13. Piret P., Meunier-Piret J., Verbist J. and Van Meerssche M., *Bull. Soc. Chim. Belges,* **81**, 539 (1972).
14. Bhattacharyya S.C. and Saha N.N., *J. Cryst. Mol. Struct.,* **8**, 209 (1978).
15. Dega-Szafran Z., Kosturkiewicz Z., Nowak E., Petryna M. and Szafran M., *J. Mol. Struct.,* **613**, 37 (2002).
16. Dega-Szafran Z., Petryna M., Tykarska E. and Szafran M., *J. Mol. Struct.*, **643**, 69 (2002).
17. Dega-Szafran Z., Dulewicz E. and Petryna M., *J. Mol. Struct.*, **651–653**, 635 (2003).
18. Dega-Szafran Z., Petryna M., Szafran M. and Tykarska E., *J. Mol. Struct.,* in press.
19. Barczyński P., Dega-Szafran Z., Dulewicz E., Petryna M. and Szafran M., *Polish J. Chem.,* **74**, 1149 (2000).
20. Headley A.D., Corona R.E. and Cheung E.F., *J. Phys. Org. Chem.,* **10**, 898 (1997), and references citted therein.
21. Beilstein Handbuch der Organischen Chemie, **20**, 59, Verlag, Springer, Berlin (1935).
22. Kuma KM4 CCD, Software, version 161, Wrocław, Poland, 1999.
23. Sheldrick G.M, SHELXS-90, *Program for the Solution of Crystal Structures*, University of Göttingen, Germany, 1990.
24. Sheldrick G.M, SHELXL-97, *Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, 1997.
25. Stewart J.J.P., *J. Comput. Chem*., **10**, 221 (1989).
26. AMPAC 6.0, Semichem, Shawnee, KS 66216, USA, 1998.
27. *International Tables for Crystallography.* Vol A. The International Union of Crystallography. Reidel D. Publishing Company, Dortrecht, Holland, 1983. P. 105.
28. Duax W.A. and Norton D.A., *Atlas of Steroid Structures*. Plenum Press, NY, 1975.
29. Donohue J., in Rich A., Davison N. (Eds), *Structural Chemistry and Molecular Biology,* Freeman, San Francisco, 1968, pp. 443–465.
30. Szafran M., Kowalczyk I., Katrusiak A. and Dega-Szafran Z., *J. Mol. Struct.*, **651–653**, 621 (2003).
31. Rudert R., Schulz B., Reck G., Vollhardt D. and Kriwanek J., *Acta Cryst.,* **B56**, 124 (2000).
32. Szafran M., Koput J., Dega-Szafran Z., Katrusiak A., Pankowski M. and Stobiecka K., *Chem. Phys.,* **289**, 201 (2003).
33. Dega-Szafran Z. and Szafran M., *J. Chem. Soc. Perkin Trans. 2*., 195 (1982).
34. Dega-Szafran Z., Antkowiak A., Grundwald-Wyspiańska M., Nowak E. and Kosturkiewicz Z., *J. Mol. Struct.,* **605**, 309 (2002).
35. Dega-Szafran Z., Katrusiak A. and Szafran M., *J. Mol. Struct.,* **555**, 203 (2000).
36. Dega-Szafran Z., Gdaniec M., Grundwald-Wyspiańska M., Kowalczyk I. and Szafran M., *J. Mol. Struct.,* **322**, 297 (1994).
37. Dega-Szafran Z., Jaskólski M., Szafran M. and Dulewicz E., *J. Mol. Struct.,* **615**, 33 (2002).
38. Szafran M., Kowalczyk I. and Barczyński P., *Israel J. Chem*., **39**, 253 (1999).
39. Emsley J., *Chem. Soc. Rev.,* **9**, 91 (1980).