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Hydrogen bonds and conformational analysis of bis(1-methylisonicotinate) hydrochloride monohydrate by X-ray diffraction, vibrational spectra and B3LYP calculations

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Abstract

In the crystal structure of bis(1-methylisonicotinate) hydrochloride monohydrate, $(MIN)_2H\cdot Cl\cdot H_2O$, 1-methylisonicotinate betaines are hemiprotonated and form a homoconjugated cation through a short asymmetric O·H·O hydrogen bond of length 2.456(3) Å. Water molecules and Cl^- anions are linked alternatively by hydrogen bonds of lengths 3.202(3) and 3.282(2) Å into planar zigzag chains along the [*c*] direction. The Cl^- anion additionally interacts electrostatically with two positively charged nitrogen atoms of the neighboring MIN molecules. The most stable conformers of $(MIN)_2H\cdot Cl\cdot H_2O$, $(MIN)_2H\cdot Cl$, $(MIN)_2H\cdot H_2O$ and $(MIN)_2H$ have been analyzed by the B3LYP/6-31G(d,p) calculations in order to determine the influence of the anion and water molecule on the hydrogen bond in the homoconjugated MIN·H·MIN unit. The FTIR spectrum of $(MIN)_2H\cdot Cl\cdot H_2O$ shows a broad and intense absorption in the 1500–400 cm^{-1} region, typical for short hydrogen bonds. The bands at 3416 and 3378 cm^{-1} confirm the presence of medium–strong hydrogen bonds between water molecules and Cl^- anions.

Keywords: 1-Methylisonicotinate betaine; Hydrogen bond; Electrostatic interactions; X-ray diffraction; DFT calculations; Conformation; FTIR and Raman spectra

1. Introduction

Pyridine carboxylic acids (picolinic, nicotinic and isonicotinic) on methylation are converted into betaines, homarine (2-carboxy-1-methylpyridinium inner salt), trigonelline (3-carboxy-1-methylpyridinium inner salt) and 4-carboxy-1-methylpyridinium inner salt. The first two betaines, homarine and trigonelline have been isolated from various plants, seeds and animal tissues [1–3]. Because of their basic nature they form 1:1 and 2:1 crystalline complexes with mineral acids [4–6].

Previously, we have described the 2:1 complexes of trigonelline with perchloric [5] and hydrochloric [6] acids, which crystallize with one water molecule. In this work, we study the 2:1 complex of 4-carboxy-1-methylpyridinium inner salt with hydrochloric acid, $(MIN)_2H\cdot Cl\cdot H_2O$, which also crystallizes with water, using X-ray diffraction, FTIR and Raman spectra. The relative energies and optimized geometries of some of the most stable conformers of $(MIN)_2H\cdot Cl$, $(MIN)_2H$ and their monohydrates are obtained from the B3LYP/6-31G(d,p) calculations. The aim of this study is to determine the influence of Cl^- anion and H_2O molecule on the hydrogen bond in the crystal and in isolated entities.

2. Experimental

2.1. Synthesis

4-Carboxy-1-methylpyridinium iodide. A solution of nicotinic acid (15 g) in methanol (70 cm^3) and methyl iodide (26 g) was heated at 70 °C in a sealed tube for 40 h. Yellow crystals were filtered off and washed with a small amount of acetone. The filtrate was evaporated to dryness under reduced pressure and the solid residue was washed with acetone. Both fractions of the crystals were combined and recrystallized from methanol, total yield 61%, m.p. 243 °C; ref. [7], m.p. 189–191 °C.

4-Carboxy-1-methylpyridinium inner salt monohydrate (betaine). 4-Carboxy-1-methylpyridinium iodide (10 g) was dissolved in water (20 cm^3) in a small canonical flask, propylene oxide (2.6 g) was added slowly, closed with a cork and left for 3 days. To remove iodopropanols, the reaction

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solution was extracted six times with equal volumes of diethyl ether, than evaporated under reduced pressure to dryness, the residue was recrystallized from methanol and white crystals were filtered off, m.p. 291 °C; ref. [7], m.p. 288 °C.

4-Carboxy-1-methylpyridinium chloride. 4-Carboxy-1-methylpyridinium inner salt monohydrate (betaine) (5 g) was dissolved in hydrochloric acid, the solution was evaporated to dryness under reduced pressure, and the white solid residue was recrystallized from methanol with one drop of hydrochloric acid, m.p. 226–228 °C; ref. [8], m.p. 265 °C.

Bis(1-methylisonicotinate) hydrochloride monohydrate was obtained by recrystallization of stoichiometric amounts of MIN·H_2O and MINHCl from a small amount of methanol, m.p. 215–217 °C. ^{1}H NMR (D_2O): δ (ppm) = 4.84 s, N^+CH_3, 8.87 d, H(2,6), 8.29 d, H (3,5); ^{13}C NMR (D_2O): δ (ppm) = 50.9 N^+CH_3, 148.5 C(2,6), 129.5 C(3,5), 153.8 C(4), 170.9 COO.

2.2. Measurements

FTIR spectra were recorded in Nujol and Fluorolube suspensions at a 2 cm^{-1} resolution on a Bruker IFS 113v spectrometer, which was evacuated to avoid water and CO_2. Each spectrum consists of 250 scans at 31 °C. Raman spectrum was recorded on a Nicolet Magna 760 spectrometer operating at the 1064 nm excitation line of an Nd:YAG laser.

The X-ray diffraction measurements were carried out using a KUMA-4 CCD diffractometer. The structure was solved by direct methods with SHELXS-97 [9] program and refined by the full-matrix least squares on F^2 data using the SHELLXL-97 [10] program. The crystal data and details concerning data collection and structure refinement are given in Table 1. Atomic coordinates and equivalent displacement parameters are listed in Table 2. Parameters in the CIF form are available as Electronic Supplementary Publication from Cambridge Crystallographic Data Centre (CCDC 273451).

Table 1
Crystal data and structure refinement for bis(1-methylisonicotinate) hydrochloride monohydrate

Empirical formula	$C_{14}H_{17}ClN_2O_5$
Formula weight	328.75
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*Cc*
Unit cell dimensions	$a = 24.791(5)$ Å $b = 7.8099(16)$ Å $c = 8.1154(16)$ Å $\beta = 97.26(3)°$
Volume	1558.7(5) Å^3
Z	4
Calculated density	1.401 g/cm^3
$F(000)$	688
Crystal size	0.3×0.3×0.1 mm
θ range for data collection	2.74–29.81°
Limiting indices h,k,l	$-33 \leq h \leq 32$, $-10 \leq k \leq 10$, $-11 \leq l \leq 8$
Reflections collected/unique/[R(int)]	7482/2601 [R(int) = 0.0436]
Completeness to $\theta = 29.81$	91.7%
Absolute structure parameter	0.46(15)
Data/restraints/parameters	2601/7/213
Goodness-of-fit on F^2	1.181
Final $R1/R2$ indices [$I > \sigma((I)$]	$R1 = 0.0478$, $wR2 = 0.1223$
R indices (all data)	$R1 = 0.0712$, $wR2 = 0.1565$
Largest diff. peak and hole	0.547 and -0.683 e Å^{-3}

Table 2
Fractional atomic coordinates and equivalent isotropic displacement parameters bis(1-methylisonicotinate) hydrochloride monohydrate. U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor

Atom	x	y	z	U(eq)
N(1)	0.4834(1)	1.3036(5)	−0.4315(5)	0.037(1)
C(2)	0.5035(2)	1.1493(6)	−0.4617(7)	0.042(1)
C(3)	0.4783(2)	1.0031(6)	−0.4195(6)	0.039(1)
C(4)	0.4322(2)	1.0151(5)	−0.3420(5)	0.032(1)
C(5)	0.4119(2)	1.1752(5)	−0.3134(6)	0.039(1)
C(6)	0.4387(2)	1.3187(6)	−0.3590(6)	0.039(1)
C(7)	0.5131(2)	1.4553(6)	−0.4754(8)	0.058(1)
C(8)	0.4047(2)	0.8538(6)	−0.2944(6)	0.044(1)
O(1)	0.3642(1)	0.8792(4)	−0.2144(4)	0.048(1)
O(2)	0.4229(2)	0.7165(5)	−0.3260(8)	0.082(1)
N(1′)	0.2070(2)	0.1833(5)	0.0912(5)	0.036(1)
C(2′)	0.1859(2)	0.3362(6)	0.1192(7)	0.043(1)
C(3′)	0.2110(2)	0.4824(6)	0.0763(6)	0.039(1)
C(4′)	0.2580(2)	0.4724(5)	0.0031(5)	0.032(1)
C(5′)	0.2788(2)	0.3125(6)	−0.0257(7)	0.039(1)
C(6′)	0.2532(2)	0.1677(6)	0.0211(7)	0.041(1)
C(7′)	0.1784(2)	0.0252(6)	0.1385(8)	0.056(1)
C(8′)	0.2856(2)	0.6352(6)	−0.0447(6)	0.041(1)
O(1′)	0.3261(1)	0.6104(4)	−0.1228(4)	0.051(1)
O(2′)	0.2682(2)	0.7719(5)	−0.0041(7)	0.085(2)
O(w)	0.6068(2)	1.1942(5)	0.2908(5)	0.070(1)
Cl	0.5866(1)	1.2051(1)	−0.1066(2)	0.047(1)
H(1)	0.3430	0.7500	−0.1800	0.0220(50)
H(2)	0.5352	1.1415	−0.5120	0.050
H(3)	0.4921	0.8964	−0.4430	0.047
H(5)	0.3803	1.1862	−0.2635	0.046
H(6)	0.4253	1.4269	−0.3389	0.047
H(71)	0.5301	1.4382	−0.5740	0.075
H(72)	0.5399	1.4913	−0.3863	0.075
H(73)	0.4856	1.5418	−0.4957	0.075
H(2′)	0.1540	0.3432	0.1680	0.051
H(3′)	0.1962	0.5888	0.0965	0.047
H(5′)	0.3101	0.3029	−0.770	0.046
H(6′)	0.2676	0.0600	0.0046	0.049
H(71′)	0.1599	0.0436	0.2341	0.072
H(72′)	0.2053	−0.0626	0.1624	0.072
H(73′)	0.1525	−0.0097	0.0464	0.072
H(1w)	0.6070(30)	1.2250(60)	0.1880(20)	0.084
H(2w)	0.6030(30)	1.0950(30)	0.3370(50)	0.084

2.3. Calculations

The calculations were performed using the GAUSSIAN 03 package [11] at the B3LYP [12,13] level of theory in conjunction with the 6-31G(d,p) [14] basis set.

3. Results and discussion

3.1. Molecular parameters

The structure of $(MIN)_2H\cdot Cl\cdot H_2O$ with the atom numbering is shown in Fig. 1, the molecular packing in the crystal in Fig. 2 and the environment of the chloride ion in Fig. 3. The bond lengths, bond angles, and torsion angles are listed in Tables 3 and 4. Two molecules of MIN are bridged by a proton to form a homoconjugated cationic system with a short, asymmetrical O–H···O hydrogen bond with the O···O distance of 2.456(3) Å. Because the hydrogen bonded MIN molecules are not symmetrically equivalent, the $(MIN)_2H$ cation is similar to the pseudo-Type A acid salts of carboxylic acids [15], $(TRG)_2H\cdot ClO_4\cdot H_2O$ [5], $(TRG)_2H\cdot Cl\cdot H_2O$ [6] and bis(quinoline betaine) hydrogen perchlorate [16]. Slightly shorter hydrogen bonds exist in the Type A acid salts of aromatic monocarboxylic acids [15] and 2:1 complexes of betaines with mineral acids [17–19], where proton is in the middle of the bridge. The $(TRG)_2H$ cations are arranged approximately parallel in the crystal lattice, as shown in Fig. 2. The two carboxy-fragments participating in the hydrogen bonding are planar, with the

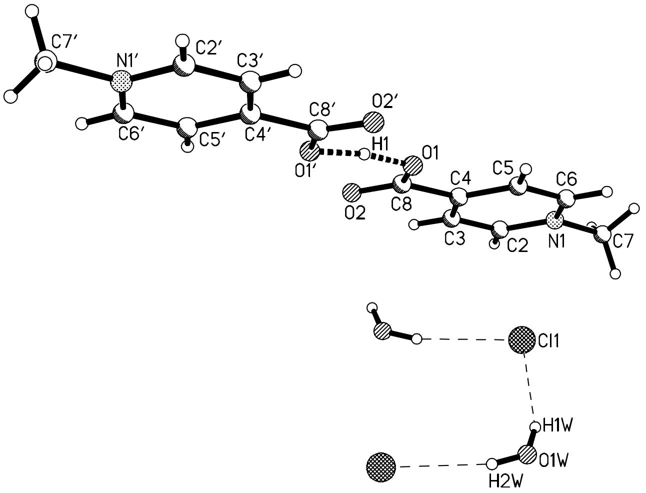

Fig. 1. View of bis(1-methylisonicotinate) hydrochloride monohydrate, $(MIN)_2H\cdot Cl\cdot H_2O$, and its atom labeling scheme.

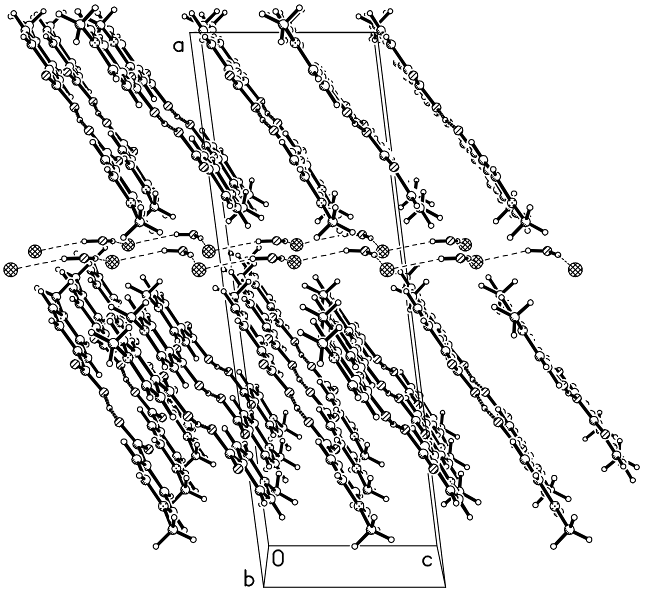

Fig. 2. Auto stereogram of the crystal structure of $(MIN)_2H\cdot Cl\cdot H_2O$. Hydrogen bonds linking the water molecules and chloride anions into chains are marked with the dashed line.

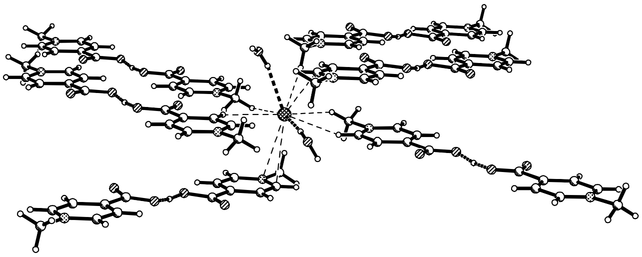

Fig. 3. The environment of the chlorine ion in bis(1-methylisonicotinate) hydrochloride monohydrate.

Table 3
Experimental bond lengths (Å) and angles (deg) for bis(1-methylisonicotinate) hydrochloride monohydrate

Bond lengths			
N(1)–C(2)	1.340(6)	N(1′)–C(2′)	1.335(6)
N(1)–C(6)	1.325(6)	N(1′)–C(6′)	1.347(6)
N(1)–C(7)	1.462(6)	N(1′)–C(7′)	1.498(6)
C(2)–C(3)	1.367(6)	C(2′)–C(3′)	1.366(6)
C(3)–C(4)	1.375(6)	C(3′)–C(4′)	1.376(6)
C(4)–C(5)	1.377(6)	C(4′)–C(5′)	1.382(6)
C(4)–C(8)	1.505(6)	C(4′)–C(8′)	1.518(6)
C(5)–C(6)	1.377(6)	C(5′)–C(6′)	1.373(6)
C(8)–O(1)	1.279(6)	C(8′)–O(1′)	1.267(6)
C(8)–O(2)	1.203(6)	C(8′)–O(2′)	1.212(6)
Bond angles			
C(2)–N(1)–C(6)	121.0(4)	C(2′)–N(1′)–C(6′)	121.7(4)
C(2)–N(1)–C(7)	118.2(4)	C(2′)–N(1′)–C(7′)	119.0(4)
C(6)–N(1)–C(7)	120.8(4)	C(6′)–N(1′)–C(7′)	119.3(4)
N(1)–C(2)–C(3)	120.7(4)	N(1′)–C(2′)–C(3′)	120.2(4)
C(2)–C(3)–C(4)	119.5(4)	C(2′)–C(3′)–C(4′)	120.7(4)
C(3)–C(4)–C(5)	118.7(4)	C(3′)–C(4′)–C(5′)	118.6(4)
C(3)–C(4)–C(8)	119.3(4)	C(3′)–C(4′)–C(8′)	119.8(4)
C(5)–C(4)–C(8)	121.9(4)	C(5′)–C(4′)–C(8′)	121.6(4)
C(4)–C(5)–C(6)	119.6(4)	C(4′)–C(5′)–C(6′)	120.1(4)
N(1)–C(6)–C(5)	120.4(4)	N(1′)–C(6′)–C(5′)	119.3(4)
O(2)–C(8)–O(1)	125.9(5)	O(2′)–C(8′)–O(1′)	127.0(5)
O(1)–C(8)–C(4)	114.3(4)	O(1′)–C(8′)–C(4′)	114.3(4)
O(2)–C(8)–C(4)	119.8(5)	O(2′)–C(8′)–C(4′)	118.8(5)
Torsion angles			
N(1)–C(2)–C(3)–C(4)	−1.3(7)	N(1′)–C(2′)–C(3′)–C(4′)	0.3(8)
N(1)–C(6)–C(5)–C(4)	0.6(8)	N(1′)–C(6′)–C(5′)–C(4′)	1.8(8)
C(2)–N(1)–C(6)–C(5)	−0.1(7)	C(2′)–N(1′)–C(6′)–C(5′)	−1.2(8)
C(6)–N(1)–C(2)–C(3)	0.4(7)	C(6′)–N(1′)–C(2′)–C(3′)	0.2(7)
C(7)–N(1)–C(2)–C(3)	178.4(5)	C(7′)–N(1′)–C(2′)–C(3′)	−179.6(5)
C(7)–N(1)–C(6)–C(5)	−178.0(5)	C(7′)–N(1′)–C(6′)–C(5′)	178.5(5)
C(2)–C(3)–C(4)–C(5)	1.9(7)	C(2′)–C(3′)–C(4′)–C(5′)	0.2(7)
C(2)–C(3)–C(4)–C(8)	−179.5(4)	C(2′)–C(3′)–C(4′)–C(8′)	179.8(4)
C(3)–C(4)–C(5)–C(6)	−1.5(7)	C(3′)–C(4′)–C(5′)–C(6′)	−1.2(7)
C(8)–C(4)–C(5)–C(6)	179.8(4)	C(8′)–C(4′)–C(5′)–C(6′)	179.1(5)
C(3)–C(4)–C(8)–O(1)	176.1(4)	C(3′)–C(4′)–C(8′)–O(1′)	−174.7(4)
C(5)–C(4)–C(8)–O(1)	−5.3(7)	C(5′)–C(4′)–C(8′)–O(1′)	4.9(6)
C(3)–C(4)–C(8)–O(2)	−0.8(7)	C(3′)–C(4′)–C(8′)–O(2′)	6.5(7)
C(5)–C(4)–C(8)–O(2)	177.8(5)	C(5′)–C(4′)–C(8′)–O(2′)	−173.7(5)

Table 4
Hydrogen bonds geometry in bis(1-methylisonicotinate) hydrochloride, its cation and their monohydrates

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)
***1** X-ray*				
O(1)–H···O(1′)	1.19(4)	1.28(4)	2.456(3)	171(3)
O(1w)–H(1w)···Cl	0.87(7)	2.38(5)	3.202(3)	161
O(1w)–H(2w)···Cl[a]	0.87(7)	2.43(6)	3.282(2)	165(5)
B3LYP/6–31G**				
***2** Linear*				
O(1)–H···O(1′)	1.053	1.450	2.501	174.4
***3** Bent*				
O(1)–H···O(1′)	1.040	1.489	2.526	174.0
O(w)–H(1w)···Cl	0.077	2.390	2.557	170.3
O(w)–H(2w)···O(2′)	0.974	2.033	2.971	172.8
***4** Linear*				
O(1)–H···O(1′)	1.205	1.208	2.413	178.3
***5** Bent*				
O(1)–H···O(1′)	1.023	1.516	2.520	164.9
***6** Linear*				
O(1)–H···O(1′)	1.137	1.289	2.425	177.5
***7** Bent*				
O(1)–H···O(1′)	1.011	1.602	2.596	166.4
O(1w)–H(w)···O(2′)	0.982	1.760	2.730	168.9
***8** Linear*				
O(1)–H···O(1′)	1.031	1.484	2.512	175.5
***9** Bent*				
O(1)–H···O(1′)	1.060	1.428	2.485	174.0

Symmetry code [a]*x*, 2−*y*, 0.5+*z*.

dihedral angle between the O(2)–C(8)–O(1) and O(12)–C(18)–O(11) moieties being 8.3(5)°, respectively. The dihedral angle between the planes through the rings is 1.2(3)° and those between the rings and the COO$^-$ moieties are 3.3(3) and 5.9(3)°, respectively, for the protonated and unprotonated 1-methylisonicotinates.

Each water molecule links two adjacent Cl$^-$ anions via two different hydrogen bonds (O(w)–H(1w)···Cl$^-$(1) of 3.202(3) Å) and (O(w)–H(2w)···Cl$^-$(1) of 3.282(2) Å) forming planar, zigzag chains along the [*c*] direction (Fig. 2). The Cl$^-$ anion additionally interacts via Coulombic attractions with two close positively charged nitrogen atoms and has close contacts with some C–H groups (Fig. 3). The shortest contacts are: Cl$^-$···N$^+$(1) of 3.517 Å, Cl$^-$···N$^+$(1′) = 4.187 Å, O(w)···N$^+$(1) of 5.114 Å and O(w)···N$^+$(1) of 3.400 Å (Table 5). In the crystal each Cl$^-$ anion and each N$^+$ atom are fourfold coordinated. A prototype of this kind of interaction has been found in tetramethylammonium halides [20], where each X$^-$ anion is tetrahedrally surrounded by four N$^+$ atoms, and each N$^+$ atom by four X$^-$ anions. The N$^+$ atoms in (MIN)$_2$H·Cl·H$_2$O are surrounded by two Cl$^-$ anions and two water molecules, while Cl$^-$ anions are surrounded only by two N$^+$ atoms, because the other two contacts are blocked by two H-bonds with water molecules.

3.2. B3LYP calculations

Table 6 shows the abbreviations of the complexes investigated, their energies, relative energies, dipole moments and conformations In Fig. 4 the X-ray and the optimized molecules are compared. Linear and bent types of conformers can be distinguished. There are three important features that contribute to the stability of the single molecules investigated

Table 5
Selected distances between the oppositely charge atoms (Å) in bis(1-methylisonicotinate) hydrochloride monohydrate determined by X-ray diffraction

	Å	Symmetry code
N(1)···Cl	3.519	*x*, *y*, *z*
	4.919	*x*, 3−*y*, −0.5+*z*
	5.026	*x*, 2−*y*, −0.5+*z*
N(1)···O(1)	4.914	*x*, *y*, *z*
	3.787	*x*, 2−*y*, −0.5+*z*
N(1)···O(2)	4.933	*x*, *y*, *z*
	3.703	*x*, 1+*y*, *z*
	3.364	*x*, 2−*y*, −0.5+*z*
	5.318	*x*, 2−*y*, 0.5+*z*
N(1)···O(w)	4.110	*x*, 2−*y*, −0.5+*z*
	5.131	*x*, 3−*y*, −0.5+*z*
	5.156	*x*, *y*, *z*
N(1)···O(1′)	4.068	*x*, 2−*y*, −0.5+*z*
N(1)···O(2′)	5.326	*x*, 2−*y*, −0.5+*z*
N(1′)···Cl	4.188	*x*−0.5, 1.5−*y*, 0.5+*z*
	4.922	*x*−0.5, −1.5+*y*, *z*
	5.185	*x*−0.5, −1.5+*y*, *z*
N(1′)···O(1)	4.044	*x*, 1−*y*, 0.5+*z*
N(1′)···O(1′)	3.869	*x*, 1−*y*, 0.5+*z*
N(1′)···O(2′)	3.677	*x*, −1+*y*, *z*
	3.458	*x*, 1−*y*, 0.5+*z*
N(1′)···O(w)	3.392	*x*−0.5, 1.5−*y*, −0.5+*z*

Table 6
Numbers, conformations, energies (Hartree), relative energies (kcal/mol) and dipole moments (μ, Debye) of the investigated molecules

	Molecule	Method	Type	Energy (Hartree)	$E_{rel.}$	Dipole
1	H_2O (MIN·H·MIN)$^+$Cl$^-$	X-ray	Linear			
2	H_2O (MIN·H·MIN)$^+$Cl$^-$	B3LYP	Linear	−1489.565787	22.876	31.9170
3	(MIN·H·MIN)$^+$Cl$^-$·H_2O	B3LYP	Bent	−1489.600242	0	8.1784
4	(MIN·H·MIN)$^+$H	B3LYP	Linear	−952.747915	0	0.4505
5	(MIN·H·MIN)$^+$H	B3LYP	Bent	−952.745718	1.38	12.0883
6	(MIN·H·MIN)$^+$$H_2O$	B3LYP	Linear	−1029.187396	0.33	2.1332
7	(MIN·H·MIN)$^+$$H_2O$	B3LYP	Bent	−1029.187928	0	13.8815
8	(MIN·H·MIN)$^+$Cl$^-$	B3LYP		−1413.134995	13.8	12.3782
9	(MIN·H·MIN)$^+$Cl$^-$	B3LYP	Bent	−1413.157021	0	7.7043

(compared with the gas phase): dipole moment, hydrogen bond distance and attractive (electrostatic) interactions between the oppositely charged atoms (the positively charged nitrogen atoms and anions or water molecules). Bent complexes with small dipole moments are favored in the gas phase. In the cation, (MIN·H·MIN)$^+$, and its monohydrates the reverse trend is observed; more stable are the linear species with smaller dipole moments. In all linear complexes, the O·H·O hydrogen bonds are slightly shorter than in the bent ones, but their energies are slightly higher (Tables 6 and 7). In cations (**4** and **5**) and their monohydrates (**6** and **7**), the linear species are more stable and the O·H·O hydrogen bonds are much shorter in comparison to the bent ones. As indicated by the data in Tables 6 and 7, the stability of the optimized complexes is controlled by the electrostatic attraction between the positively charged nitrogen atoms N$^+$(1) and N$^+$(1′) and Cl$^-$ anion. In the bent complexes (**3**, **9**) both N$^+$(1)···Cl$^-$ and N$^+$(1’)···Cl$^-$ distances are short (between 3.280 and 3.867 Å), while in linear conformers (**2**, **8**) only one distance is short, but the second is longer than 10 Å.

The water molecule has also some effect on the stability of the conformers investigated. Conformer **6** (linear) is less stable than **7** (bent) by 0.33 kcal/mol. In **6** the O·H·O hydrogen bond is shorter by 0.171 Å relative to that in **7**, but the N$^+$(1′)···O(w) distance is longer by 8.399 Å.

3.3. FTIR and Raman spectra

Fig. 5 shows the FTIR, Raman and second derivative spectra of (MIN)$_2$H·Cl·H_2O. The FTIR spectrum displays a broad and strong absorption in the 1500–400 cm^{-1} region, whereas in the Raman spectrum this feature is absent. A similar broad absorption appears in the IR spectra of the 2:1 complexes of other betaines [21] and acid salts of carboxylic acids [22–24]. The broad absorption is typical of compounds with short H-bonds and arises from the stretching (strong absorption) and bending (much weaker absorption) vibrations of the O–H group involved in a short O···O hydrogen bond.

In the FTIR spectrum, the continuous absorption and the skeletal vibrations overlap, but the latter feature can be distinguished in the second-derivative spectrum, d^2 (Fig. 5b). In the second-derivative spectra, the minima have the same wavenumbers as the maxima in the absorbance spectra [25–28]. The intensity of relative amplitudes of bands in the d^2 spectra varies inversely with the square of the half-width of the absorption bands. The observed wavenumbers and their tentative assignments, based on comparison with the spectra of 4-carboxy-1-methyl-pyridinium chloride [29] and isonicotinic acid [30], are listed in Table 8. The frequency plot of the negative bands in the d^2 spectrum versus the Raman frequencies is linear with unit slope (Fig. 6). Thus the derivative spectrometry can be used to estimate frequencies of the narrow bands covered by the broad absorption due to the stretching and bending OHO vibrations.

4. Conclusions

According to the X-ray data, in the bis(1-methylisonicotinate) hydrochloride monohydrate, (MIN)$_2$H·Cl·H_2O, a pair of 1-methylisonicotinate molecules is joined by a proton to form a homoconjugated cation, featuring a short and asymmetric hydrogen bond with the O···O distance equal to 2.456(3) Å. The 1-methylisonicotinate units are not equivalent as a result of electrostatic interaction with Cl$^-$ anion and H_2O molecule. The hydrogen bond in the investigated complex is similar to that in

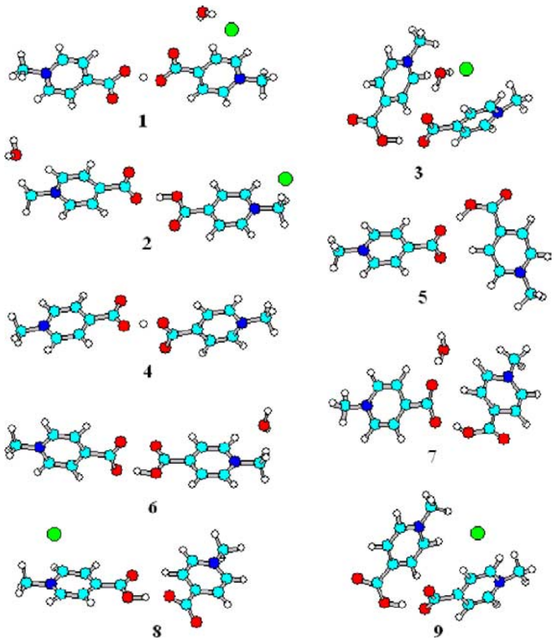

Fig. 4. Comparison of X-ray (**1**) and B3LYP (**2**–**9**) structures of bis(1-methylisonicotinate) hydrochloride, its cation and their monohydrates.

Table 7
Selected parameters (bond lengths in Ångstroms, angles in degrees) for (MIN)$_2$HCl, (MIN)$_2$H and their monohydrates

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
	Linear	Linear	Bend	Linear	Bend	Linear	Bend		Bend
O(1)···O(11)	2.456	2.501	2.526	2.413	2.520	2.425	2.596	2.512	2.485
O(1)–H	1.19	1.053	1.040	1.205	1.026	1.137	1.011	1.031	1.060
O(1′)–H	1.28	1.450	1.489	1.208	1.516	1.289	1.602	1.484	1.428
O(1)HO(1′)	171	174.4	174.0	178.3	164.9	177.5	166.4	175.5	174.0
C(8)–O(1)	1.279	1.309	1.310	1.288	1.309	1.296	1.317	1.314	1.304
C(8′)–O(1′)	1.267	1.271	1.270	1.288	1.266	1.282	1.255	1.265	1.281
C(8)–O(2)	1.203	1.222	1.218	1.226	1.216	1.223	1.214	1.227	1.221
C(8′)–O(2′)	1.212	1.235	1.245	1.226	1.245	1.229	1.255	1.236	1.235
O(1)–C(8)–O(2)	125.9	127.7	124.4	130.1	124.3	129.5	123.9	126.4	124.8
O(1′)–C(8′)–O(2′)	127.0	137.6	128.8	130.1	129.9	130.5	129.3	131.8	129.3
N(1)–C(2)–C(3)–C(4)	−1.3	0.29	−1.1	−0.12	0.5	−0.07	−0.7	1.0	−1.2
N(1′)–C(2′)–C(3′)–C(4′)	0.3	−0.01	2.0	−0.17	−0.11	0.01	0.96	−1.5	−0.8
C(2)–C(3)–C(4)–C(8)	−179.5	179.7	179.8	−179.7	175.5	−179.6	178.1	−177.1	177.6
C(2′)–C(3′)–C(4′)–C(8′)	179.8	−179.7	165.5	−179.7	178.6	−179.7	−178.5	−179.2	170.0
C(3)–C(4)–C(8)–O(1)	176.1	−1.4	34.9	−2.1	26.7	−1.75	26.2	2.4	33.7
C(3′)–C(4′)–C(8′)–O(1′)	−174.7	1.04	10.7	−2.1	−0.35	−1.33	22.1	−24.5	−11.2
C(3)–C(4)–C(8)–O(2)	−0.8	178.4	−143.1	177.8	−151.4	178.3	−151.8	−180.0	−144.3
C(3′)–C(4′)–C(8′)–O(2′)	6.5	−179.1	−163.9	177.8	−179.9	178.7	−157.7	156.9	174.7
O(2)–C(8)–O(1)–H		1.33	−165.1	−6.3	−167.4	−5.8	−165.9	2.0	−166.3
O(2′)–C(8′)–O(1′)–H		3.19	10.6	−6.4	33.2	−5.7	7.8	−88.2	18.5
N(1)···Cl		3.694	3.843					3.084	3.867
N(1′)···Cl		14.057	3.280					10.050	3.310
N(1)···OH$_2$		14.979	2.954			3.715	4.235		
N(1′)···OH$_2$		3.747	4.799			14.387	5.988		

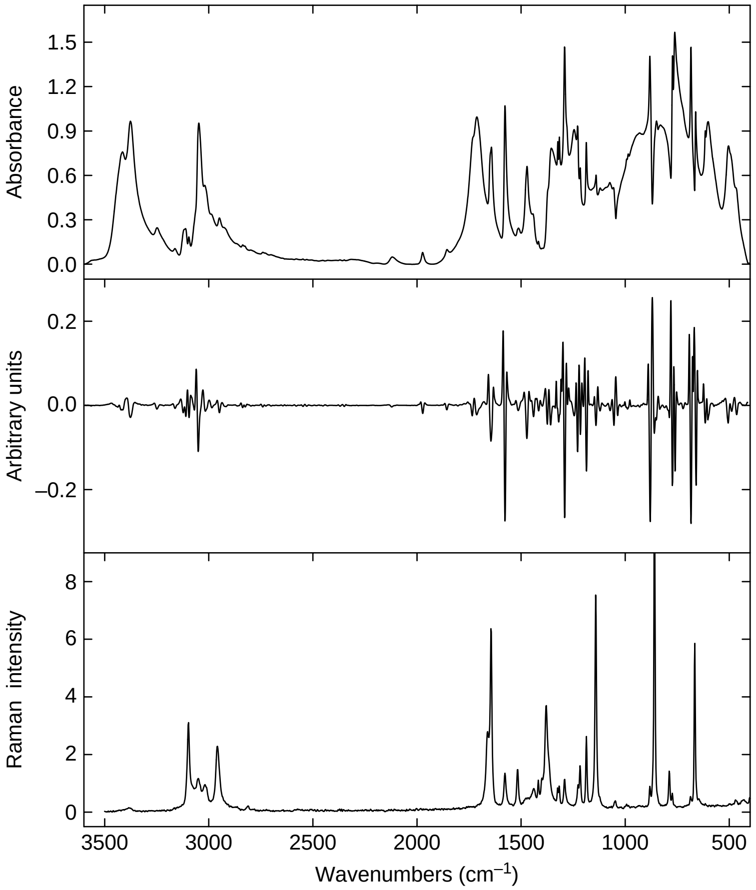

Fig. 5. Vibrational spectra: (a) FTIR spectra (suspension in Nujol and Fluorolube) of (MIN)$_2$H·Cl·H$_2$O; (b) second derivative FTIR spectrum and (c) Raman spectrum.

Table 8
Vibrational frequencies of 4-carboxy-1-methylpyridinium inner salt monohydrate, MIN·H_2O, its hydrochloride, MINH·Cl(t) and bis(1-methylisonicotinate) hydrochloride monohydrate, $(MIN)_2HCl\cdot H_2O$

MIN·H_2O	MINH·Cl[a]	$(MIN)_2HCl\cdot H_2O$			Approximate assignments
FTIR	FTIR	Raman	FTIR	d^2	
				3436	H_2O
				3422	H_2O
3420			3414	3413	H_2O
			3376	3377	H_2O
			3248	3249	H_2O
			3162	3161	$\nu\mathrm{CH}$
	3118			3122	$\nu\mathrm{CH}$
3107			3112	3111	$\nu\mathrm{CH}$
3093	3100	3098	3096	3095	$\nu\mathrm{CH}$
	3080			3070	$\nu\mathrm{CH_3}$
3038	3053	3050	3048	3050	$\nu\mathrm{CH_3}$
		3019	3020	3018	$\nu\mathrm{CH_3}$
				2983	$\nu\mathrm{CH_3}$
		2959	2949	2949	$\nu\mathrm{CH_3}$
	2668–2214				$\nu\mathrm{OH}$
	1710		1712	1712	$\nu\mathrm{CO}$
1653		1661			$\nu_{as}\mathrm{COO}$
1637	1646	1644	1643	1645	$\nu\mathrm{CC}$
1604					$\nu\mathrm{CC}$
1565	1585	1577	1577	1577	$\nu\mathrm{CC}$
	1519	1517	1512	1512	$\nu\mathrm{CC}+\nu\mathrm{CN}$
				1472	$\nu\mathrm{CC}+\nu\mathrm{CN}$
	1460	1439		1441	$\beta\mathrm{CH_3}$
		1417	1417	1416	$\beta\mathrm{CH_3}$
	1400	1400		1398	$\beta\mathrm{OH}$
1363		1380	1354	1375, 1358	$\beta\mathrm{CH_3}$
1315	1320	1324	1324	1337	$\beta\mathrm{CH_3}$
1304		1317	1316	1320, 1305	$\beta\mathrm{CH_3}$
1291	1288	1291	1290	1291	$\nu\mathrm{CC}+\nu\mathrm{CO}+\beta\mathrm{OH}$
	1257		1245	1245	$\beta\mathrm{CH}$
	1245	1226	1228	1228	$\beta\mathrm{CH}$
	1207	1217	1216	1215	$\beta\mathrm{CH}+\nu\mathrm{CN}$
1185	1192	1186	1187	1200	$\beta\mathrm{CH}$
	1140	1141	1140	1141	$\beta\mathrm{CH}+\nu\mathrm{CC}$
	1131		1120	1120	$\beta\mathrm{CH}$
	1075		1074	1072	$\beta\mathrm{CH_3}+\nu\mathrm{CN}$
	1060	1047		1054	$\beta\mathrm{CH_3}+\nu\mathrm{CN}$
1040	1042			1036	β Ring
900	927				
881	878	881	881	897	β Ring + $\nu\mathrm{CN}$
857	864	859		860	β Ring + $\nu\mathrm{CN}$
	846		850	849	β Ring + $\nu\mathrm{CN}$
784	769	788	772	778, 774	β Ring + $\nu\mathrm{CN}$
	751	772	762	761	$\tau\mathrm{CO_2}$
689	676	686	684	684, 673	τ Ring
664	667	666	662	660	β Ring
615	612		615	615	β Ring + $\beta\mathrm{CO}$
535	515		504	505	τ Ring + $\beta\mathrm{CO}$
	475	470		488	τ Ring + $\gamma\mathrm{CN}$
463				464	τ Ring + $\gamma\mathrm{CN}$

[a] Data from Ref. [29]. d^2—second derivative frequencies.

pseudo-Type A acid salts of carboxylic acids and it can be described by a potential energy function with a double minimum. Each of the water molecules and Cl^- anions are hydrogen bonded and form planar zigzag chains.

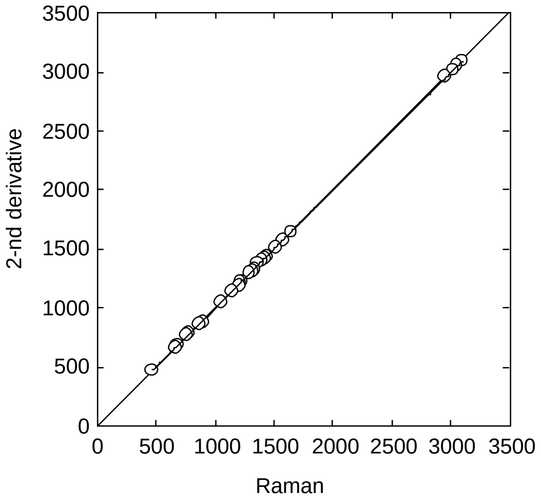

Fig. 6. Relation between d^2 and Raman frequencies for $(MIN)_2H\cdot Cl\cdot H_2O$; $\nu(d^2) = 3.0243 + 0.9980\ \nu(\mathrm{Raman})$, $r = 0.9998$.

Two conformer types (linear and bent) of $(MIN)_2H\cdot Cl$ and $(MIN)_2H$ and their monohydrates have been analyzed by the B3LYP/6-31G(d,p) calculations. Their stability depends on: (i) dipole moment, (ii) hydrogen bond length, and (iii) attractive (electrostatic) interactions between the oppositely charged atoms (the positively charged nitrogen atoms and Cl^- anions).

The FTIR spectrum of the complex shows a very broad absorption, typical of such short hydrogen bonds. In the Raman spectrum only narrow bands are present since the O·H·O stretching vibration is not active. The frequencies of the negative bands in the second derivative spectrum agree well with the Raman frequencies. Derivative spectrometry can be used to estimate the frequencies of the narrow bands covered by the broad absorption due to the stretching and bending OHO vibrations.

Acknowledgements

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