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Structure of 3,4-dicarboxy-1-methylpyridinium chloride studied by X-ray diffraction, DFT calculations, NMR and FTIR spectra

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ABSTRACT

The structure of 3,4-dicarboxy-1-methylpyridinium chloride (34DCMPCl) has been studied by X-ray diffraction, DFT calculations, NMR and FTIR spectra. The crystals are monoclinic, space group $P2_1$. Chloride anion links two 3,4-dicarboxy-1-methylpyridinium cations into infinite zigzag chains down [0 1 0] by the $OH\cdots Cl^-\cdots HO$ hydrogen bonds of 2.953(2) and 2.968(2) Å. Hydrogen bonds in single molecules optimised by the B3LYP/6-31G(d,p) approach depend on the environment. In vacuum (**2** and **3**) the hydrogen bonded proton is linked with chloride atom ($Cl–H\cdots O$), while in DMSO (**4**) the structure is similar to that in the crystal ($Cl\cdots H–O$). Linear correlations between the experimental ^{13}C and ^1H chemical shifts (δ_{exp}) of the investigated compound in DMSO-d_6 and the calculated GIAO/B3LYP/6-31G(d,p) magnetic isotropic shielding tensors (σ_{calc}) using the screening solvation model (COSMO), $\delta_{exp} = a + b\ \sigma_{calc}$, are reported. The FTIR spectrum of the solid compound is consistent with the X-ray structure. The deformation absorptions in plane and out of plane, both in FTIR and second-derivative spectra (d^2), appear as two bands and confirm the $OH\cdots Cl^-\cdots HO$ hydrogen bonds formation.

1. Introduction

3,4-Pyridinedicarboxylic acid (cinchomeronic acid) is zwitterionic (betaine) in the solid state, with one acid hydrogen transferred to the ring nitrogen atom [1]. Each molecule of the acid is involved in intermolecular hydrogen bonds with four neighbouring molecules, twice as proton donors, $O(1)–H\cdots O(4)$ of 2.514 Å (symmetry code: $1 - x$, $y - 0.5$, $2.5 - z$) and $N(1)–H\cdots O(3)$ of 2.664 Å (symmetry code: $x - 0.5$, $0.5 - y$, $1 - z$) and twice as proton acceptors $O(4)\cdots H–O(1)$ of 2.514 Å (symmetry code: $1 - x$, $y + 0.5$, $1 - z$) and $O(3)\cdots H–N(1)$ of 2.664 Å (symmetry code: $x + 0.5$, $0.5 - y$, $1 - z$) to form a complex spiral arrangement in the crystal [1]. The carbonyl oxygen atom O(2) is free from the hydrogen bond involvement.

The crystal structure of 2,3-pyridinedicarboxylic acid (quinolinic acid) is different. One of the acid hydrogens is also located on the ring nitrogen atom, but carboxyl and carboxylate groups are involved in the intramolecular O·H·O hydrogen bond of 2.398(3) Å [2,3], which is comparable with some acid salts of carboxylic acid [4].

The term betaine, which has been originally used to denote the trimethylated derivative of glycine, $Me_3N^+–CH_2–COO^-$, now is commonly applied to all the internal quaternary ammonium, sulphonium or phosphonium molecules [5–8]. Betaines are compounds with oppositely charged centers and are often referred to as zwitterions, dipolar ions or inner salts. An interesting group of betaines are 1-methyl derivatives of various pyridine carboxylic acids prepared by methylation of the acid with methyl iodide [9,10] or methyl sulfate [11] followed by treatment with propylene oxide [12,13] or ion-exchange resins, Dowex-22C [10,13] or Amberlite [9]. These betaines form 1:1 and 2:1 complexes with mineral acids [14–16].

In our earlier works, we have described the structures of homarinium chloride [17], trigonellinium chloride [18] and 4-carboxy-1-methylpyridinium chloride [19]. This paper continues our structural and vibrational studies of hydrogen bonded complexes, and is focused on 3,4-dicarboxy-1-methylpyridinium chloride (34DCMPCl).

2. Experimental and calculations

2.1. 3,4-Dicarboxy-1-methylpyridinium iodide

To a solution of 3,4-pyridinedicarboxylic acid (15 g) in methanol (20 cm^3) methyl iodide (26 g) was added and heated at 70 °C in a sealed tube for 40 h. Yellow crystals were filtered off and washed with small amount of acetone. The filtrate was evaporated to dryness under reduced pressure and the solid residue was washed with acetone. Both fraction of crystals were combined and recrystallized from methanol, total yield 44%, m.p. 230–233 °C.

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2.2. 3,4-Dicarboxy-1-methylpyridinium chloride

3,4-Dicarboxy-1-methylpyridinium iodide (9 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 4 days. To remove iodopropanol, the reaction solution was extracted six times with equal volumes of diethyl ether, then evaporated under reduced pressure to dryness, the residue was recrystallized from water and white crystals of 3,4-dicarboxy-1-methylpyridinium inner salt were filtered off, total yield 19%, m.p. 218–222 °C. The crude inner salt (3 g) was dissolved in hydrochloric acid, the solution was evaporated to dryness under reduced pressure, and the yellow solid residue was recrystallized from methanol, m.p. 236 °C (dec.).

2.3. Measurements and calculations

The X-ray diffraction measurements were carried out on a KUMA KM4-CCD diffractometer [20]. The structure was solved by direct methods with the SHELXS-97 program [21]. All hydrogen atoms were derived from a difference Fourier map. The structure was refined by the full-matrix least-squares method on F^2 using the SHELXL-97 program [22]. All atoms were included in the refinement with anisotropic (non-H atoms) and isotropic (H atoms) displacement parameters. The crystal data, together with the details concerning the data collection and structure refinement are given in Table 1 and the atomic coordinates in Table 2. The molecular structure and atom numbering of 34DCMPCl are shown in Fig. 1. The parameters in the CIF form are available as Electronic Supplementary Information from the Cambridge Crystallographic Database Centre (CCDC 733905). Molecular illustrations were prepared using ORTEPII [23] and the XP [24] packages.

FTIR spectra were recorded in Nujol and Fluorolube mulls on a Bruker IFS 66v/S spectrometer, evacuated to avoid water and CO_2 absorptions, at a 2 cm^{-1} resolution. Each FTIR spectrum consisted of 64 scans.

The ^1H and ^{13}C NMR spectra were recorded in DMSO-d_6 solution relative to internal TMS on a Varian Gemini 300 VT spectrometer operating at 300.07 and 75.46 MHz for proton and carbon-13, respectively. The chemical shifts were confirmed by COSY and HETCOR experiments.

Table 1
Crystal data and structure refinement for 3,4-dicarboxy-1-methylpyridinium chloride, 34DCMPCl.

Empirical formula	$C_8H_8ClNO_4$
Formula weight	217.60
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	a = 6.5422(8) Å
	b = 11.1459(10) Å
	c = 12.9279(9) Å
	β = 116.116(17)°
Volume	461.43(17) $Å^3$
Z	2
Calculated density	1.566 g/cm^3
Absorption coefficient	0.401 mm^{-1}
$F(0\,0\,0)$	224
Crystal size	0.34 × 0.22 × 0.12 mm
θ range for data collection	3.22°–28.85°
Max/min indices h, k, l	$-7 \leqslant h \leqslant 8$, $-14 \leqslant k \leqslant 14$, $-9 \leqslant l \leqslant 7$
Reflections collected/unique	3161/2132 [R(int) = 0.0126]
Completeness to θ_{max} = 28.85°	94.3%
Refinement method	Full-matrix-block least-squares on F^2
Data/restraints/parameters	2132/1/135
Goodness-of-fit on F^2	1.077
Final $R1/wR2$ indices [$I > 2\sigma(I)$]	0.0531/0.1361
$R1/wR2$ indices (all data)	0.0609/0.1395
Absolute structure parameter	−0.08(10)
Largest diff. peak and hole	0.995 and −0.302 e $Å^{-3}$

Table 2
Atomic coordinates (×10^4) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for 3,4-dicarboxy-1-methylpyridinium chloride, 34DCMPCl. U_{eq} (U_{iso} for H-atoms) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}/U_{iso}
Cl(1)	16221(1)	−902(1)	8301(1)	38(1)
N(1)	3520(5)	−2182(3)	1825(4)	32(1)
C(2)	3653(5)	−980(4)	1914(5)	28(1)
C(3)	5714(6)	−414(3)	2962(5)	32(1)
C(4)	7685(5)	−1085(3)	3976(5)	30(1)
C(5)	7473(6)	−2336(3)	3887(6)	37(1)
C(6)	5394(7)	−2860(3)	2797(7)	37(1)
C(7)	1289(7)	−2786(4)	633(7)	44(1)
C(8)	5792(6)	929(4)	3130(6)	33(1)
C(9)	10047(6)	−588(3)	4951(6)	36(1)
O(1)	4039(5)	1443(3)	1568(5)	53(1)
O(2)	7279(5)	1458(2)	4556(5)	49(1)
O(3)	11244(4)	−938(4)	6852(4)	51(1)
O(4)	10725(5)	23(3)	3901(5)	47(1)
H(2)	2333	−525	1258	33
H(5)	8757	−2812	4575	45
H(6)	5274	−3692	2726	44
H(71)	1503	−3640	721	66
H(72)	648	−2541	−821	66
H(71)	274	−2567	1229	66
H(3)	12860(80)	−890(50)	6900(70)	49(11)
H(1)	4270(140)	2050(90)	1750(130)	110(30)

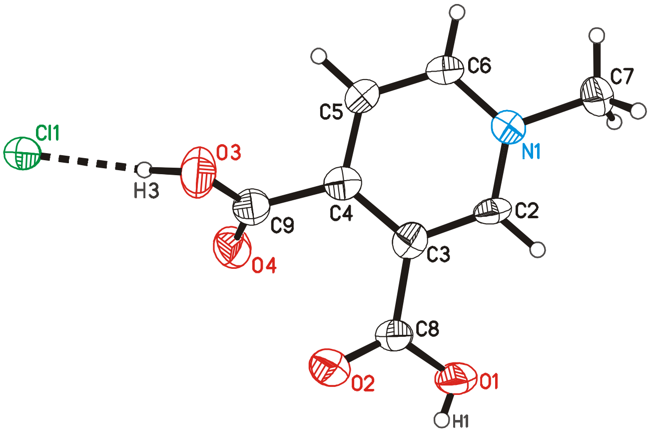

Fig. 1. Atomic numbering for 3,4-dicarboxy-1-methylpyridinium chloride (34DCMPCl). The hydrogen bond is indicated by the dashed line, and the thermal ellipsoids are shown at the 50% probability level.

The calculations of geometrical parameters were performed using the Gaussian 03 program package [25], COSMO model [26] and B3LYP [27,28] approach in conjunction with the 6-31G(d,p) basis set [29] without any symmetry restrictions. The magnetic isotropic shielding tensors were calculated using the standard GIAO/B3LYP/6-31G(d,p) (Gauge-Independent Atomic Orbital) approach with the Gaussian 03 program package.

3. Results and discussion

3.1. Crystal structure

The molecular structure and atom numbering of 3,4-dicarboxy-1-methylpyridinium chloride (34DCMPCl) are shown in Fig. 1. The