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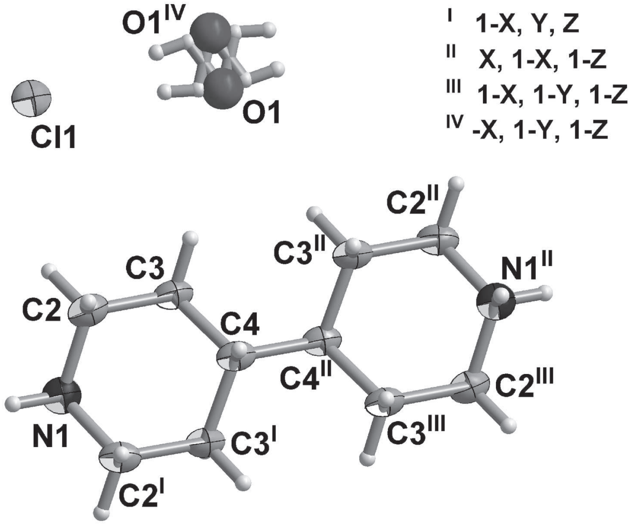
Paweł Socha and Lukasz Dobrzycki*

Crystal structure of 4,4′-bipiperidinium dichloride 0.12 hydrate, $C_{10}H_{22}N_2Cl_2 \cdot 0.12\ H_2O$



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Abstract

$C_{10}H_{22.24}Cl_2N_2O_{0.12}$, orthorhombic, *Cmca* (no. 64), $a = 9.6661(8)$ Å, $b = 7.3063(6)$ Å, $c = 19.3270(15)$ Å, $V = 1364.94(19)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0359$, $wR_{ref}(F^2) = 0.1009$, $T = 170$ K.

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The crystal structure is shown in the figure. Tables 1–3 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

Single crystals of title compound were obtained during slow evaporation from HCl acidify aqueous solution of 4,4′-bipiperidine.

Table 1: Data collection and handling.

Crystal:	Colourless, prism, size 0.12×0.16×0.19 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	4.48 cm^{-1}
Diffractometer, scan mode:	Bruker Kappa APEX II CCD, ω scan
$2\theta_{max}$:	59.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7177, 105
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 881
$N(param)_{refined}$:	44
Programs:	Bruker programs [2], SHELX [3], Diamond [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1N)	8*f*	0.5000	0.607(4)	0.273(2)	0.053
H(2N)	8*f*	0.5000	0.744(5)	0.324(1)	0.053
H(2A)	16*g*	0.3676	0.4131	0.3373	0.045
H(2B)	16*g*	0.2901	0.6056	0.3285	0.045
H(3A)	16*g*	0.2878	0.5103	0.4457	0.043
H(3B)	16*g*	0.3670	0.7014	0.4374	0.043
H(4)	8*f*	0.5000	0.3519	0.4513	0.037
O(1)	8*d*	0.048(3)	0.5000	0.5000	0.047(8)
H(1X)	16*g*	−0.0411	0.4939	0.5202	0.070
H(2X)	16*g*	0.0341	0.5142	0.4517	0.070

Experimental details

All H atoms connected to C atoms were refined as rigid model with C—H distances equal to 0.99 Å and isotropic thermal parameters 1.2 greater than U_{eq} of corresponding C atoms. Positions of two hydrogen atoms at protonated amino groups were refined and their isotropic thermal parameters were set to be 1.5 U_{eq}(N). Atomic displacement parameter of the water oxygen atom was refined using isotropic model. Occupancy of the water molecule was free to refine yielding 0.0298(24). Hydrogen atoms at the water molecule were modelled to have both O—H distances equal to 0.95 Å and H—O—H angle of 106°. The water molecule was model in the way that one O—H···Cl hydrogen bond to be formed. Positions of these H atoms were not refined (AFIX 3) and their isotropic

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***Corresponding author: Lukasz Dobrzycki,** Faculty of Chemistry, University of Warsaw, Pasteura 1, PL-02093 Warsaw, Poland, e-mail: dobrzyc@chem.uw.edu.pl
Paweł Socha: Faculty of Chemistry, University of Warsaw, Pasteura 1, PL-02093 Warsaw, Poland

Table 3: Fractional atomic coordinates and displacement parameters (Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl(1)	8*f*	0	0.54706(6)	0.33947(2)	0.0380(3)	0.0237(2)	0.0448(3)	0	0	−0.0011(2)
N(1)	8*f*	0.5	0.6252(2)	0.3181(1)	0.0387(9)	0.0237(7)	0.0434(9)	0	0	−0.0026(6)
C(4)	8*f*	0.5	0.4865(2)	0.4608(1)	0.0245(8)	0.0205(7)	0.046(1)	0	0	−0.0009(7)
C(2)	16*g*	0.3724(2)	0.5450(2)	0.34865(7)	0.0292(7)	0.0344(7)	0.0494(8)	−0.0005(5)	−0.0041(5)	−0.0023(6)
C(3)	16*g*	0.3715(1)	0.5692(2)	0.42638(7)	0.0242(6)	0.0358(6)	0.0479(8)	0.0015(5)	−0.0010(5)	0.0004(5)

temperature parameters were set to be 1.5 times greater than U_{iso} of the corresponding O atom.

Discussion

4,4′-bipiperidine and its dication can serve as a building block in solid state similarly as widely known 4,4′-bipyridinium moiety [1]. However due to its aliphatic character the pack of both cations has to be different. Here we present the structure of 4,4′-bipiperidine dihydrochloride non-stoichiometric hydrate. The asymmetric unit of the title structure consists of one quarter of a 4,4′-bipiperidine dication located on the $2/m$ site, one half of a chloride anion positioned at the mirror plane and 0.02 of disordered water molecule located on the 2-fold axis near centre of inversion (Figure). The amount of disordered water molecules per one dication yields 0.12. The water molecule is positioned between two equidistant Cl^- ions with $Cl^- \cdots O$ contacts and $Cl^- \cdots O \cdots Cl^-$ angle yielding 3.156(4) Å and 163.2(9)°, respectively with no other potential HB acceptors present. The other neighboring atoms of the disordered water molecule are only aliphatic hydrogen atoms of the cations. In such case only one $O \cdots Cl^-$ hydrogen bond can be formed whereas the other H atom has to stay non-bonded. Thus such position is not so attractive for water molecule. This is the reason why non-stoichiometric number of water molecules is present in the unit cell. Such a small amount of the solvent results in relatively low density of the ionic crystal equal to 1.185 g/cm^{-3} while the density of 4,4′-bipyridinium dihydrochloride salt yields 1.518 g/cm^{-3}, see reference [1]. Non-efficient packing can also play role in the behavior of the salt below 170 K – it undergoes a phase transitions with damaging the single crystal. In the crystal lattice symmetrically related aliphatic piperidinium rings of the cations have the chair-like conformation. In the structure $NH^+ \cdots Cl^-$ hydrogen bonds can be found (two for each NH_2^+ group) equal to 3.098(2) Å and 3.110(2) Å for $(x+1/2, y, -z+1/2)$ and $(x+1/2, y+1/2, z)$ symmetry related Cl1 ions, respectively. These hydrogen bonds link Cl^- anions and the cations in layers perpendicular to (100). In these layers disordered and partial occupancy H_2O molecules are weakly anchored.

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