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8-Aminoquinolinium Chloride Dihydrate

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Abstract

The title compound, $C_9H_9N_2^+.Cl^-.2H_2O$, crystallized from water as pale-orange plates. The structure reveals strong hydrogen bonding between one of the water molecules and both the quinolinium [N—H⋯O 2.691 (4) Å] and amino [N—H⋯O 2.967 (4) Å] H atoms. The second water molecule is hydrogen bonded to the first [O—H⋯O 2.658 (3) Å], and weakly to two different chloride ions. The overall packing results in stacks of quinolinium ions, with adjacent molecules having opposite orientations.

Comment

We are interested in the magnetic behavior of compounds with the general formula $(AH)_2MX_4$, where A is an organic base, M is a 2+ transition metal ion and X is a halide. Previous work by ourselves (Albrecht *et al.*, 1998) and others (Place & Willett, 1987a,b; Luque *et al.*, 1997) has shown that these compounds may pack in such a fashion as to yield low-dimensional magnetic lattices, where the magnetic exchange is mediated by van der Waals contacts between the halides. The nature of the packing is determined by the size and shape of

the organic base. Examination of the structures of the hydrohalide salts of these bases has sometimes proved useful in predicting which will generate useful magnetic lattices (Prince & Turnbull, 1996; Anagnostis & Turnbull, 1998). The study of the structure of 8-amino-quinolinium chloride dihydrate, (I), was undertaken for this purpose.
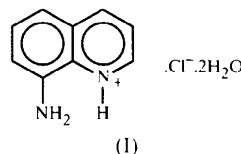
8-Aminoquinolinium chloride crystallized from water as the dihydrate in the space group $P\bar{1}$. The molecular structure is shown in Fig. 1. The quinolinium ring is planar, with the ring atoms and the amino group having a mean deviation from the plane of 0.011 (1) Å. The bond lengths within the ring are all 1.39±0.03 Å, except for the short N1—C2 bond of 1.319 (3) Å. The short bond to the amino nitrogen, 1.354 (3) Å, reflects a strong π-character on N2—C8. Similarly, the bond angles within the ring are all 120±3°, except for the enlarged C9—N1—C2 angle [123.7 (2)°] and the reduced C7—C8—C9 angle [116.3 (2)°]. The bond lengths and angles within the quinolinium ring are, in general, comparable with those reported for the dimeric silver coordination complex (Schmidbauer *et al.*, 1991). The bond lengths are also comparable with those reported for the aqua-bis(8-aminoquinoline)zinc tetrachlorozincate salt (Kerr *et al.*, 1981), while the angles only deviate significantly near the atoms involved in chelating the zinc ion (N1, C8 and C9 in the present structure). A third coordination complex of 8-aminoquinoline, involving nickel, has also been reported (Mohedano *et al.*, 1985), but comparisons there are not useful as that complex shows substantial distortions of the quinoline ring.
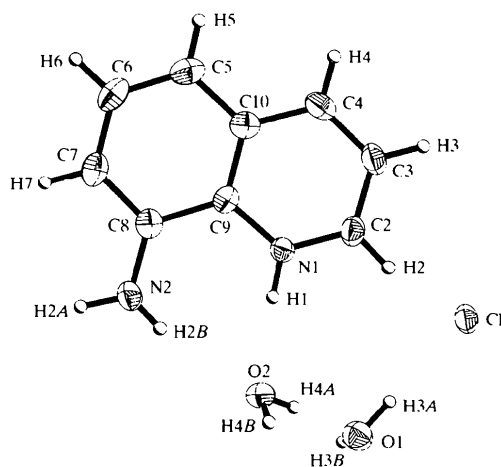

Fig. 1. The molecular structure of 8-aminoquinolinium chloride dihydrate, showing displacement ellipsoids at 50% probability.

The crystal lattice is held together by a number of significant hydrogen-bonding interactions. One water molecule (O2, H4A and H4B) is chelated to the quinolinium ring via both quinolinium and amino protons [N1—H1···O2 2.691 (4) Å and 175.3 (15)°; N2—H2B···O2 2.967 (4) Å and 167 (2)°]. This water molecule is also hydrogen bonded to the second water molecule [O2—H4A···O1 2.658 (3) Å and 172 (3)°] and to a chloride ion in an adjacent layer [O2—H4B···Cl^i 3.095 (3) Å and 164 (4)°; symmetry code: (i) $-x+2$, $-y-1$, $-z+2$]. In addition to O2, the second water molecule (O1) is more loosely hydrogen bonded to two different chloride ions [O1—H3A···Cl^{ii} 3.180 (6) Å and 164 (4)°; O1—H3B···Cl 3.107 (4) Å and 174 (4)°; symmetry code: (ii) $-x+1$, $-y-1$, $-z+2$]. This hydrogen bonding results in the formation of four-, five-, six- and eight-membered rings in the lattice (not counting the H atoms; see Fig. 2).
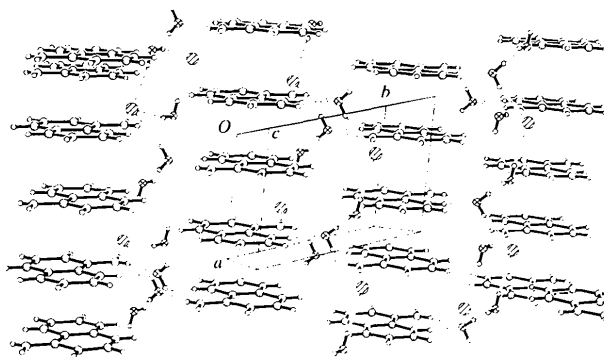

Fig. 2. Packing diagram of 8-aminoquinolinium chloride dihydrate, showing ring formation via hydrogen bonding.

An additional effect of the lattice arrangement is to stack the quinoline rings such that the normal to the plane is 3° from the a axis (Fig. 2). The orientation of the rings alternates down the stack such that adjacent rings have their amino groups directed 9.4° away from the +b or −b directions, similar to the stacking of the pyridine rings observed in the structure of bis(2-amino-5-chloropyridinium) tetrabromocuprate (Albrecht et al., 1998). Based upon this similarity, we anticipate that the 8-aminoquinolinium ion will prove useful in the preparation of low-dimensional magnetic lattices. The synthesis of these complexes is in progress.

Experimental

Crystals of (I) were grown by dissolving 8-aminoquinoline in 0.5 M HCl and allowing slow evaporation of the solution. Diffraction quality crystals were collected and air-dried.

Crystal data

$C_9H_9N_2^+.Cl^-.2H_2O$
$M_r = 216.66$
Triclinic
$P\bar{1}$
$a = 6.7710 (10)$ Å
$b = 8.630 (4)$ Å
$c = 9.880 (3)$ Å
$\alpha = 103.88 (2)°$
$\beta = 102.80 (2)°$
$\gamma = 100.14 (3)°$
$V = 530.3 (3)$ Å^3
$Z = 2$
$D_x = 1.357$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 16 reflections
$\theta = 4.72–12.45°$
$\mu = 0.34$ mm^{-1}
$T = 158 (2)$ K
Irregular plate
$0.70 \times 0.55 \times 0.25$ mm
Orange

Data collection

Siemens $P4$ diffractometer
ω scans
Absorption correction:
empirical via ψ scans (Siemens, 1990)
$T_{min} = 0.765$, $T_{max} = 0.919$
2222 measured reflections
1834 independent reflections
1492 reflections with $I > 2\sigma(I)$

$R_{int} = 0.096$
$\theta_{max} = 25°$
$h = -7 \rightarrow 1$
$k = -9 \rightarrow 9$
$l = -11 \rightarrow 11$
3 standard reflections
every 97 reflections
intensity decay: 2.97%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.115$
$S = 1.036$
1834 reflections
155 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0762P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.006$
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}
Extinction correction: none
Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

N1—C2	1.319 (3)	C8—C9	1.427 (3)
N1—C9	1.373 (3)	C9—C10	1.411 (3)
N1—H1	0.88 (3)	O1—H3A	0.86 (6)
N2—C8	1.354 (3)	O1—H3B	0.78 (4)
N2—H2A	0.83 (3)	O2—H4A	0.88 (3)
N2—H2B	0.78 (3)	O2—H4B	0.76 (3)
C7—C8	1.390 (3)		
C2—N1—C9	123.7 (2)	C6—C7—C8	121.9 (2)
C2—N1—H1	114.2 (15)	N2—C8—C7	121.1 (2)
C9—N1—H1	122.2 (15)	N2—C8—C9	122.6 (2)
C8—N2—H2A	117.3 (19)	C7—C8—C9	116.3 (2)
C8—N2—H2B	123 (2)	N1—C9—C10	117.7 (2)
H2A—N2—H2B	120 (3)	N1—C9—C8	120.5 (2)
N1—C2—C3	120.2 (2)	C10—C9—C8	121.8 (2)

After locating all the non-H atoms, the aromatic H atoms were placed in fixed positions with a riding model. The H atoms on the quinoline nitrogen (H1), the amino group (H2A and H2B) and the water molecules (H3A/H3B and H4A/H4B) were located on the difference map, and their coordinates and isotropic displacement parameters refined.

Data collection: XSCANS (Siemens, 1992). Cell refinement: XSCANS. Data reduction: SHELXTL/PC (Siemens, 1990). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL/PC. Software used to prepare material for publication: SHELXTL/PC.

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Comment

Keto carboxylic acids offer options for varying the pattern of dimeric hydrogen bonding that dominates functionally unadorned acids. Most often, the ketone fails to participate, resulting in typical carboxyl dimers, but less commonly, intermolecular carboxyl–ketone hydrogen bonds occur, yielding a catemer. A third, rare, arrangement has an internal hydrogen bond, while two instances are known of acid–ketone dimerization, and several cases are known of hydrates with more complex hydrogen-bonding patterns. In addition, we have recently reported an instance of carboxyl catemerization, not previously observed in keto acids (Lalancette *et al.*, 1998), and we have cited and discussed numerous examples of these hydrogen-bonding modes (Thompson *et al.*, 1992; Coté *et al.*, 1996).

We report here the structure and hydrogen-bonding behavior of the title δ-keto acid, (I). This category of keto acids embraces examples of dimeric and internal hydrogen bonds, as well as both anhydrous and hydrated catemers. Compound (I) was of particular interest to us as the next-highest homolog of (±)-2,3-dihydro-3-oxo-1H-indenecarboxylic acid. The crystal structures for both the anhydrous and hydrated forms of this lower homolog, the former of which displays a homochiral (screw-related) catemeric hydrogen-bonding pattern, have been reported recently (Lalancette *et al.*, 1997).

(I)

(±)-4-Oxo-1,2,3,4-tetrahydronaphthalene-1-carboxylic Acid: Hydrogen Bonding and Carboxyl Disordering in a δ-Keto Acid

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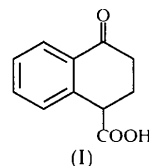
Abstract

The crystal structure of the title compound ($C_{11}H_{10}O_3$) contains hydrogen-bonded centrosymmetric carboxyl dimers. Significant carboxyl disorder was found, and was modeled by two rotational conformers, yielding two O···O distances of 2.649 (14) and 2.666 (17) Å.

Our analysis of (I) reveals that the carboxyl group is disordered, both rotationally and with respect to bond lengths and angles, and is turned approximately orthogonal to the plane of the aromatic ring, with the mean carboxyl plane producing a dihedral angle of 77.6 (4)° with the aromatic ring. Fig. 1 shows a centrosymmetric dimer pair and depicts the modeled rotational disorder of the acid group. The two O···O distances, one for each rotational conformer, are: $O3···O2^i$ = 2.649 (14) and $O3'···O2'^i$ = 2.666 (17) Å [symmetry code: (i) $-x$, $1-y$, $-z$]. A single molecule of this pair constitutes the asymmetric unit, and its numbering is shown. The flexible ketone ring adopts a conformation resembling a folded envelope, which allows the ketone to lie in the plane of the aromatic ring [torsion angle O1—C4—C4a—C5 = 0.8 (3)°], and which positions the carboxyl group pseudo-equatorially [torsion angle C9—C1—C2—C3 = −176.4 (2)°].

For highly ordered dimeric carboxyls, typical values cited for the C—O bond lengths and C—C—O angles are 1.21, 1.31 Å and 123, 112° (Borthwick, 1980).