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Key indicators

Single-crystal X-ray study
T = 130 K
Mean σ(C–C) = 0.002 Å
R factor = 0.040
wR factor = 0.103
Data-to-parameter ratio = 10.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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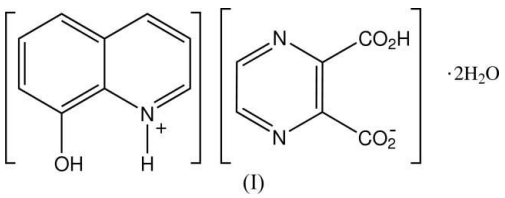
The asymmetric unit of the title compound, $C_9H_8NO^+\cdot C_6H_3N_2O_4^-\cdot 2H_2O$, contains two independent cations, two anions and four water molecules of solvation. A three-dimensional framework structure is formed through extensive hydrogen-bonding involving most donor and acceptor species. Significant aromatic C—H···O and cation–cation π–π interactions are also present.

Comment

8-Quinolinol (8-hydroxyquinoline = 8-HQ) is a versatile bidentate complexing analytical reagent known as oxine and with pH control is capable of selectively forming complexes with most metal ion species (Skoog *et al.*, 1988). As a Lewis base, the hetero-N of 8-HQ may be readily protonated (pK_{a1} = 4.9 and pK_{a2} = 10.9) and with carboxylic acids, monocations usually result, the majority of reported structures being those of the expected 1:1 salts, *e.g.* with 3,5-dinitrobenzoic acid and 3,5-dinitrosalicylic acid (Smith *et al.*, 2001) and Kemp's triacid (Smith *et al.*, 2000). Compound adducts are also known, the most common being those in which 8-HQ is the adduct molecule *e.g.* in the metal complexes $K^+\cdot$8-$HQ^-\cdot n$(8-HQ) (where n = 1, 2) (Hughes & Truter, 1979). However, in the proton-transfer salts with 4-nitrobenzoic acid (4-NBA), (8-$HQ^+\cdot$4-$NBA^-\cdot$4-NBA) (Smith *et al.*, 2001), salicylic acid (SA), (8-$HQ^+\cdot SA^-\cdot$SA) (Jebamony & Muthiah, 1998) and dibromosuccinic acid (DBSA), [2(8-HQ^+)·$DBSA^{2-}\cdot$2(DBSA)] (Li *et al.*, 2005), the adduct molecule is the acid species. The salicylic acid compound is formed in a solid-state reaction (Singh *et al.*, 2000) but differs from the 2:2 proton-transfer non-adduct tetrameric compound formed under similar solid-state conditions (Smith *et al.*, 2003).



(I)

The aromatic carboxylic acid used in this present work, pyrazine-2,3-dicarboxylic acid (PDCA), has proved to be useful for co-crystal formation and the structures of its proton-transfer compounds with the aromatic Lewis bases 3-hydroxypyridine (Lynch *et al.*, 1994), creatinine (Smith & White, 2001) and the isomeric monoaminobenzoic acids (Lynch *et al.*, 1994; Smith *et al.*, 1995) have been reported. The structure of the title compound (I), obtained from the 1:1 stoichiometric reaction of PDCA with 8-HQ, 8-hydroxy-

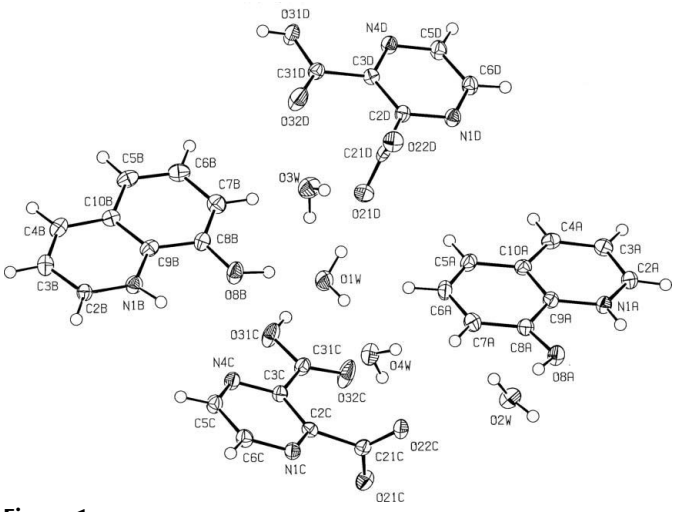


Figure 1
The molecular configuration and atom naming scheme for the two 8-HQ cations (*A* and *B*), the two PDCA anions (*C* and *D*) and the four water molecules of solvation in the asymmetric unit of (I). Displacement ellipsoids are drawn at the 50% probability level.

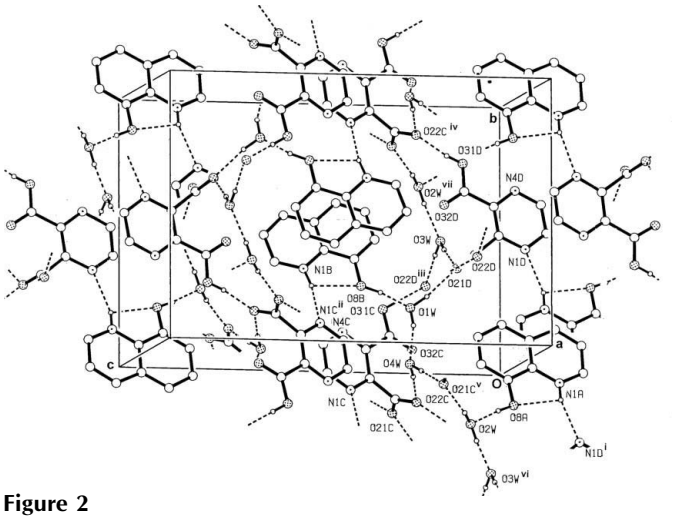


Figure 2
A perspective view of the packing, showing hydrogen-bonding associations as dashed lines. [Symmetry codes: (vi) $x+1, y-1, z$; (vii) $x-1, y+1, z$; for other symmetry codes, see Table 1.]

quinolinium 3-carboxypyrazine-2-carboxylate dihydrate, (I), is reported here.

In (I), the asymmetric unit contains two 8-HQ$^+$ cations (*A* and *B*), two PDCA$^-$ monoanions (*C* and *D*) and four water molecules of solvation (Fig. 1). There are only minor conformational differences in the carboxylate and carboxylic acid substituent groups in anions *C* and *D* [torsion angles C3—C2—C21—O21 = −80.4 (2) (*C*) and 85.6 (2)° (*D*); C2—C3—C31—O31 = 177.85 (16) (*C*) and 177.93 (15)° (*D*)]. The hydrogen-bonding interactions associated with all cation and anion species are also similar (Table 1), giving a three-dimensional framework structure (Fig. 2). The interactions include the usual intramolecular hydrogen bond in the 8-HQ cations [N1···O8 = 2.6891 (19) and 2.6946 (19) Å], single N$^+$—H···N(hetero) associations to both anions and strong phenolic O—H···O(water) interactions. In addition, there are significant cation–cation π–π interactions in the stacks forming along the *a*-axis direction {ring-centroid separations and inter-ring dihedral angles between the six-membered rings N1/C2/C3/C4/C10/C9 and C5–C10 are 3.465 (1) Å and 3.35 (1)° [*A* at $(-x+2, -y, -z)$], and 3.421 (1) Å and 3.32 (1)° [*B* at $(-x+1, -y+1, -z+1)$]}.

Experimental

The title compound, (I), was synthesized by heating together 1 mmol quantities of pyrazine-2,3-dicarboxylic acid and 8-quinolinol (8-hydroxyquinoline) in 50 ml of 80% ethanol–water under reflux for 10 min. After concentration to *ca* 30 ml, partial room temperature evaporation of the hot-filtered solution gave yellow crystal prisms **blocks below?** (m.p. 442.6–445.1 K).

Crystal data

$C_9H_8NO^+\cdot C_6H_3N_2O_4^-\cdot 2H_2O$
$M_r = 349.30$
Triclinic, $P\overline{1}$
$a = 6.8754$ (9) Å
$b = 12.0387$ (15) Å
$c = 19.338$ (2) Å
$\alpha = 86.138$ (2)°
$\beta = 80.977$ (2)°
$\gamma = 73.673$ (2)°
$V = 1516.6$ (3) Å^3
$Z = 4$
$D_x = 1.530$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.12$ mm^{-1}
$T = 130$ (2) K
Block, yellow
0.40 × 0.40 × 0.30 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{min} = 0.93$, $T_{max} = 0.97$
8060 measured reflections
5281 independent reflections
4475 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 25.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.103$
$S = 1.03$
5281 reflections
508 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0503P)^2 + 0.4013P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1A—H1A···O8A	0.88 (2)	2.322 (19)	2.6946 (19)	105.3 (15)
N1A—H1A···N1D^{i}	0.88 (2)	2.26 (2)	3.106 (2)	161.4 (17)
N1B—H1B···O8B	0.94 (2)	2.29 (2)	2.6891 (19)	105.0 (15)
N1B—H1B···N1C^{ii}	0.94 (2)	2.22 (2)	3.127 (2)	161.8 (18)
O8A—H8A···O2W	0.92 (2)	1.68 (2)	2.5967 (19)	175 (2)
O8B—H8B···O1W	0.90 (3)	1.66 (3)	2.5597 (19)	179 (4)
O31C—H31C···O22D^{iii}	0.90 (3)	1.68 (3)	2.5705 (18)	180 (4)
O31D—H31D···O22C^{iv}	0.84 (3)	1.76 (3)	2.5939 (17)	173 (2)
O1W—H11W···O21D	0.90 (3)	1.90 (3)	2.7750 (19)	163 (3)
O1W—H12W···O4W	0.92 (3)	1.85 (3)	2.743 (2)	164 (3)
O2W—H21W···O21C^{v}	0.89 (3)	1.92 (2)	2.7839 (19)	163 (2)
O2W—H22W···O3W^{vi}	0.87 (3)	1.90 (2)	2.753 (2)	166 (3)
O3W—H31W···O22D^{iii}	0.85 (3)	1.98 (3)	2.825 (2)	176 (2)
O3W—H32W···O21D	0.89 (3)	1.98 (3)	2.868 (2)	174 (2)

D—H···A	D—H	H···A	D···A	D—H···A
O4W—H41W···O22C	0.87 (3)	2.00 (3)	2.8637 (19)	172 (2)
O4W—H42W···O21C^{v}	0.92 (3)	1.87 (3)	2.779 (2)	178.2 (12)

Symmetry codes: (i) $-x+2, -y, -z$; (ii) $-x+1, -y, -z+1$; (iii) $x-1, y, z$; (iv) $x, y+1, z$; (v) $x+1, y, z$; (vi) $x+1, y-1, z$.

H atoms involved in hydrogen-bonding interactions were located by difference methods and their positional and isotropic displacement parameters were refined. Aromatic ring H atoms were included in the refinement in calculated positions (C—H = 0.95 Å) using a riding-model approximation, with U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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References

Bruker (1999). *SADABS* (Version 2.03) and *SAINT* (Version 6.02). Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2000). *SMART*. Version 5.55. Bruker AXS Inc., Madison, Wisconsin, USA.
Hughes, D. L. & Truter, M. R. (1979). *J. Chem. Soc. Dalton Trans.* pp. 520–527.
Jebamony, J. R. & Muthiah, P. T. (1998). *Acta Cryst.* C**54**, 539–540.
Li, D.-X., Xue, D.-J. & Xu, Y.-Z. (2005). *Acta Cryst.* E**61**, o402–o404.
Lynch, D. E., Smith, G., Byriel, K. A. & Kennard, C. H. L. (1994). *Aust. J. Chem.* **47**, 309–319.
Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*, University of Göttingen, Germany.
Singh, N. B., Singh, R. & Singh, K. (2000). *Z. Phys. Chem.* **214**, 179–186.
Skoog, D. A., Holler, D. M. & West, F. J. (1988). *Anal. Chem.*, 5th ed., pp. 76–77. New York: Saunders.
Smith, G., Lynch, D. E., Byriel, K. A. & Kennard, C. H. L. (1995). *Acta Cryst.* C**51**, 2629–2633.
Smith, G., Wermuth, U. D. & White, J. M. (2000). *J. Chem. Soc. Chem. Commun.* pp. 2349–2350.
Smith, G., Wermuth, U. D. & White, J. M. (2001). *Aust. J. Chem.* **54**, 171–175.
Smith, G., Wermuth, U. D. & White, J. M. (2003). *CrystEngComm*, **5**, 58–61.
Smith, G. & White, J. M. (2001). *Aust. J. Chem.* **54**, 97–100.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.