Syntheses, Spectral, Thermal and Structural Characterization of 2-Hydroxyanilinium and 2-Amino-3-hydroxy-pyridinium Squarates

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New salts of 2-hydroxyaniline and 2-amino-3-hydroxypyridine with squaric acid were synthesized and characterized by elemental analyses, IR spectroscopy and thermal analyses (TG, DTG and DTA). The crystal structures of bis(2-hydroxyanilinium) squarate, $[(C_6H_8NO^+)_2(C_4O_4)^{2-}]$ (**1**) and bis(2-amino-3-hydroxy-pyridinium) squarate dihydrate, $[(C_5H_7N_2O^+)_2(C_4O_4)^{2-}] \cdot 2\,H_2O$ (**2**) were determined by single crystal X-ray diffraction. Both compounds crystallize in the monoclinic system, space group $P2_1/c$. The organic ammonium squarates decompose in two thermal steps.

Key words: Squaric Acid, Squarate Salts, Thermal Analyses

Introduction

Hydrogen bonding is one of the principal intermolecular interactions that frequently play key roles in molecular recognition and self-assembly as well as in crystal engineering research [1] and has been used effectively to predict and design supramolecular assemblies in one, two and three dimensions [2, 3]. In the present work, we selected the potentially interesting squaric acid anions. These anions are useful building blocks for constructing crystalline architectures, because of the rigid and flat four-membered ring framework, and their proton donating and accepting capabilities for hydrogen bonding [4]. Squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione, $H_2C_4O_4$, H_2sq) has been of much interest because of its cyclic structure and possible aromaticity [5 – 8]. It is a strong acid (pK_1 = 1.2 – 1.7 and pK_2 = 3.2 – 3.5) and has been used to synthesize new types of organic compounds having potential application in nonlinear optics (NLO) [9, 10]. The crystal structures of hydrogen squarates with the cations derived by protonation of L-arginine [11], *R*-(–)-1-phenylglycine [12], guanidine [9], 1-phenylethylamine [13], L-(–)-asparagine [14], L-(+)-serine [15], ammonia [16], 2-aminopyrimidine, 3- and 4-aminopyridine [17], L-canavanine [18], methylamine, ethylamine, 1,3-diaminopropane, 1,4-diaminobutane, 1,5-diaminopentane, *N*,*N*′-dimethylpiperazine, *N*,*N*,*N*′,*N*′-tetramethylguanidine [19], L-prolineamide [22], 4,4′-dipyridylacetylene and 1,2-bis (4-pyridyl)ethylene [23], pyrimidine, benzodiazepine [24] are known. Furthermore the crystal structures of squarates with the cations derived by protonation of ammonia [20], 8-aminoquinoline [17], 8-hydroxyquinoline [21], bis(3-aminopropyl)ethylenediamine [25], di(2-aminopyrimidine) [26], bis(tetra-*n*-propylamine) [27] and thiurea [28] have already been published. Recently, we reported the crystal structures of dinicotinamidium squarate [29], picolinamidium squarate, di-*p*-toluidinium squarate dihydrate [30], 2-(acetylamino)-4-methylpyridinium hydrogen squarate, pyridine-2-carboxamidium hydrogensquarate, 2-methylpyridinium hydrogensquarate monohydrate, and di(2-amino-4-methylpyrimidinium) squarate [31]. As part of our ongoing research, in the present paper, we describe, the synthesis, spectroscopic properties, thermal analysis and crystal structure of 2-hydroxyanilinium squarate (**1**) and 2-amino-3-hydroxy-pyridinium squarate dihydrate (**2**). The components are shown in Fig. 1.

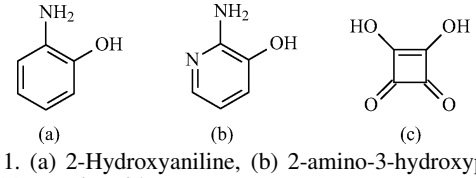

Fig. 1. (a) 2-Hydroxyaniline, (b) 2-amino-3-hydroxypyridine, (c) squaric acid.

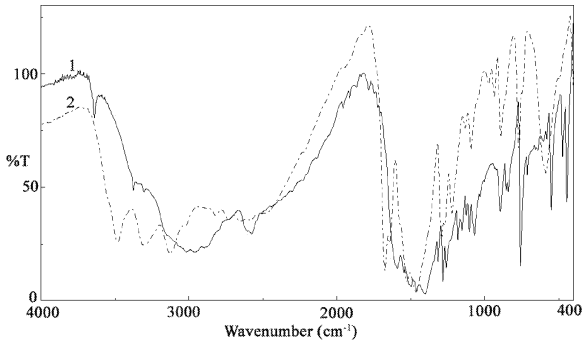

Fig. 2. IR spectra of **1** (–) and **2** (-·-·-·).

Results and Discussion

Compounds **1** and **2** were prepared by simple mixing of squaric acid and the respective amines in water/methanol mixtures at 50 °C. Crystalline materials formed after cooling the reaction mixtures to r. t.

IR spectra

The IR spectra of bis(2-hydroxyanilinium) squarate (**1**) and bis(2-amino-3-hydroxy-pyridinium) squarate dihydrate (**2**) are given in Fig. 2. They show intense bands at 3637 and 3485 cm^{-1} due to the O–H stretching vibrations of the hydrogen-bonded hydroxyl group or water molecules, respectively. In the IR spectra of **1**, the absorption bands in the frequency range 3372 – 3301 cm^{-1} are attributed to the $\nu(NH_3)$ vibrations of the 2-hydroxyanilinium ion, while in the IR spectrum of **2** the medium intensity bands at 3298 and 3130 cm^{-1} correspond to the NH_2 group and protonated pyridyl group of 2-amino-3-hydroxypyridine. The relatively weak absorption bands at 3014 – 2576 cm^{-1} for **1** and 2820 – 2657 cm^{-1} for **2** are due to the ν(C–H) vibrations. The C=N stretching mode in **2** was observed at 1676 cm^{-1}. The strong absorptions at 1593 cm^{-1} for **1** and 1529 cm^{-1} for **2** are attributed to the mixed vibrations of the squarate ring.

Thermal analyses

The thermal behaviour of the compounds was followed up to 700 °C in a static air atmosphere (Fig. 3).

The thermal decomposition of **1** and **2** is similar. For **2**, the first stage is related to the dehydration in the temperature range of 52 – 194 °C. The two moles of water molecules are released by giving an endothermic effect at 129 and 161 °C (DTG_{max}) (found 9.19, calcd. 9.73 %). The second stage, in the temperature range of 201 – 251 °C, is related to the decomposition of the 2-amino-3-hydroxypyridine molecule. This stage is followed by the decomposition of remaining 2-amino-3-hydroxypyridine and partial decomposition of squarate anions. Upon further heating the remaining organic residue starts to burn exothermically (DTG_{max} = 463 and 543 °C).

Table 1. Summary of the crystal data, details of data collection and structure determination of **1** and **2**.

	1	**2**
Chemical formula	$C_8H_8NO_3$	$C_{14}H_{14}N_4O_6x2H_2O$
Molecular weight	166.15	370.12
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
Color	brown	brown
a [Å]	9.9173(16)	3.8038(3)
b [Å]	4.9712(5)	17.291(2)
c [Å]	15.234(2)	12.0786(12)
β [deg]	99.427(13)	90.622(8)
V [Å^3]	740.89(18)	794.38(14)
Z	4	4
D_{calc} [g cm^{-3}]	1.490	1.399
Absorption coefficient μ [mm^{-1}]	0.116	0.117
θ_{max} [deg]	28.01	27.51
h, k, l limits	$-11 \le h \le 12$, $-6 \le k \le 5$, $-19 \le l \le 19$	$-4 \le h \le 4$, $-22 \le k \le 22$, $-15 \le l \le 15$
R_{int}	0.0462	0.1928
$R[F^2 \ge 2\sigma(F^2)]$	0.0378	0.0908
$wR(F^2)$	0.1061	0.2661
Goodness-of-fit on F^2	1.046	1.037
Number of refined parameters	141	155
Largest difference peak and hole [e A^{-3}]	0.18, −0.16	0.32, −0.27

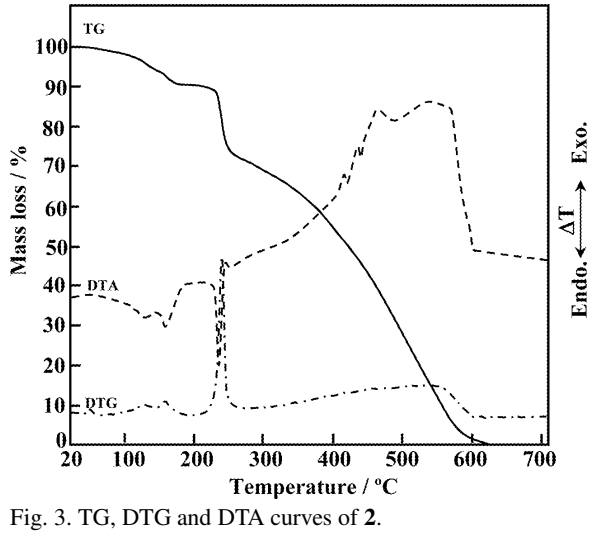

Fig. 3. TG, DTG and DTA curves of **2**.

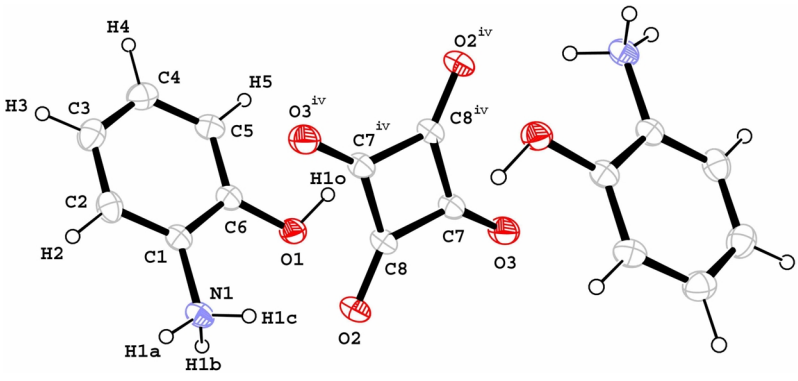

Fig. 4. The molecular structures of cations and anion in crystals of **1** and crystallographic atomic numbering scheme. Displacement ellipsoids are drawn at the 40 % probability level and H atoms are shown at small arbitrary radii (symmetry code: iv $-x+2, -y, -z+1$).

Table 2. Selected bond lengths (Å) and angles (deg) for **1**.

Bond lengths			
N1–C1	1.459 (2)	C1– C2	1.374(2)
N1–H1A	0.90 (2)	C2–C3	1.376 (3)
N1–H1B	0.94 (2)	C3–C4	1.382 (3)
N1–H1C	0.97 (2)	C4–C5	1.384 (2)
C7–C8	1.454 (2)	C5–C6	1.385 (2)
O2–C8	1.267 (2)	C6–C1	1.392 (2)
O3–C7	1.247 (2)	C6–O1	1.358 (2)
C8–C7^{i}	1.461 (2)		
Bond angles			
C1–N1–H1A	112.5 (12)	C7–C8–C7^{i}	90.61 (11)
C1–N1–H1B	110.9 (11)	C8–C7–C8^{i}	89.39 (11)
C1–N1–H1C	110.5 (13)	C6–O1–H1O	110.1 (14)

Symmetry code: ^{i} $2-x, -y, 1-z$.

Table 3. Hydrogen-bonding geometry (Å, deg) for **1**.

D–H···A	D–H	H···A	D···A	D–H···A
N1–H1A···O2^{i}	0.89 (2)	2.06 (2)	2.93 (1)	163.1 (17)
N1–H1B···O2	0.94 (2)	1.96 (1)	2.89 (1)	175.0 (15)
N1–H1C···O2^{ii}	0.97 (2)	1.83 (2)	2.76 (1)	161.5 (18)
O1–H1O···O3^{iii}	0.98 (2)	1.61 (2)	2.58 (1)	175 (2)

Symmetry codes: ^{i} $2-x, 1/2+y, 3/2-z$; ^{ii} $2-x, y-1/2, 3/2-z$; ^{iii} $2-x, -1-y, 1-z$.

Crystal structures

Details of the crystal structure of **1** are given in Table 1. Each squaric acid molecule donates one hydrogen atom to the NH_2 group of a 2-hydroxyaniline molecule, forming the bis(2-hydroxyanilinium) squarate salt, $[(C_6H_8NO)_2(C_4O_4)]$ (Fig. 4). The asymmetric unit of **1** contains one protonated 2-hydroxyanilinium cation and one-half of a centrosymmetric squarate dianion, sq^{2-}. Both ions are essentially planar, the dihedral angle between the squarate and the benzene rings is 34.96(6)°. The sq^{2-} ion has two different C–O bonds [C8–O2 = 1.266(1) Å; C7–O3 = 1.247(2) Å] which are of approximately equal length and significantly longer than normal C=O bonds [32] (Table 2). These lengths indicate a degree of electron delocalization in the sq^{2-} ion.

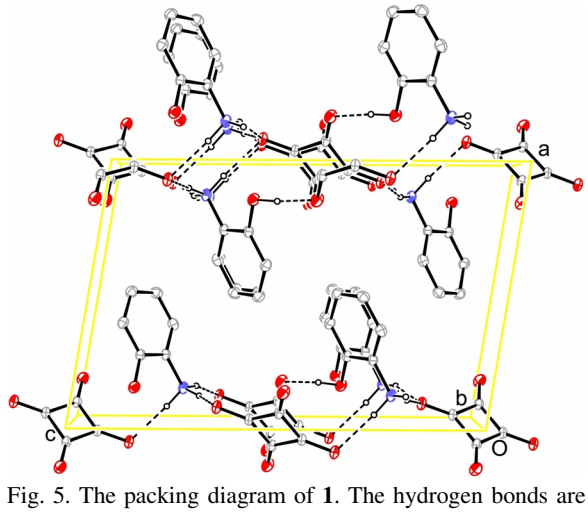

Fig. 5. The packing diagram of **1**. The hydrogen bonds are shown by the dashed lines.

Anions and cations are linked to each other by N–H···O and O–H···O hydrogen bonds as well as $\pi\cdots\pi$ interactions generating a 3D network (Table 3, Fig. 5). Two squarate oxygen atoms have hydrogen bond interactions with N atoms of three 2-hydroxyanilinium molecules, while the other O atoms of the sq^{2-} anion also form hydrogen bonds with the OH group of one 2-hydroxyanilinium molecule.

A summary of crystallographic data and refinement results for **2** are given in Table 1. Compound **2** contains two protonated 2-amino-3-hydroxy-pyridinium cations and one squarate dianion (sq^{2-}), together with two water molecules (Fig. 6). Each squaric acid molecule has donated one H atom to the N atom of a pyridine ring, forming the bis(2-amino-3-hydroxy-pyridinium) squarate dihydrate salt. The sq^{2-} ion has one C–O bond [C7–O2 = 1.323(5) Å] that is shorter than a normal single C–O bond (1.426 Å in methanol, 1.36 Å in acetic acid [32]), and one intermediate C–O bond [C6–O3 = 1.254(4) Å] that is longer than a normal

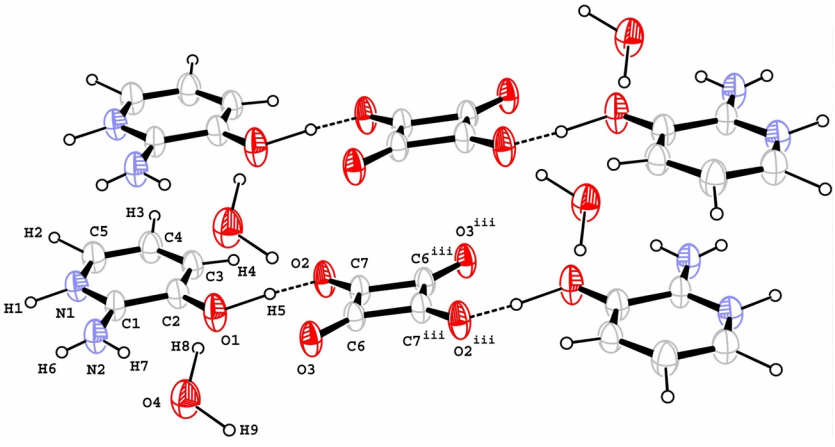

Fig. 6. Fundamental units in the crystal structure of **2** and atomic numbering scheme adopted. Displacement ellipsoids are drawn at the 50 % probability level and H atoms are shown at small arbitrary radii (symmetry code: ^{iii} $x-1, y, z$).

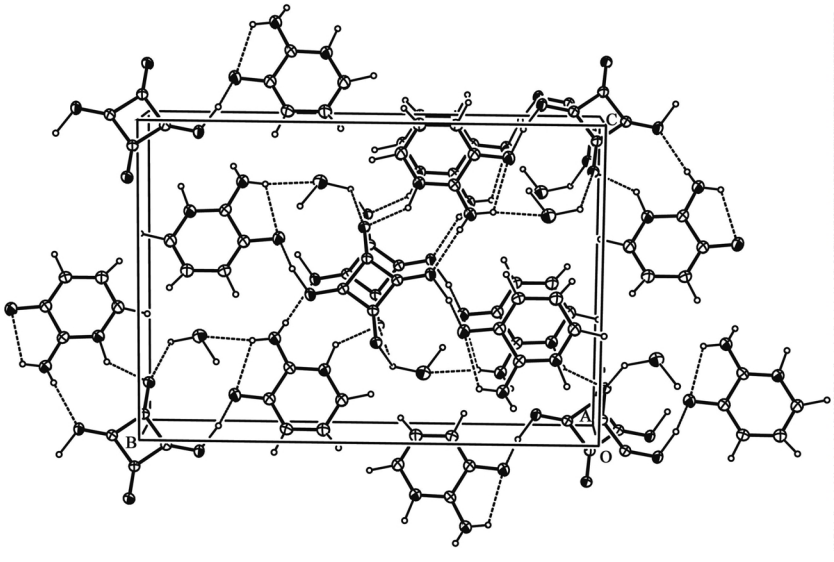

Fig. 7. The packing diagram of **2**. The hydrogen bonds are shown by dashed lines.

Table 4. Selected bond lengths (Å) and angles (deg) for **2**.

Bond lengths			
N1–C1	1.339(5)	C2–C3	1.364(6)
N1–C5	1.374(6)	C3–C4	1.394(6)
N2–C1	1.323(6)	C4–C5	1.349(7)
O1–C2	1.322(6)	C6–C7	1.455(5)
O2–C7	1.323(5)	C6–C7^{i}	1.456(5)
O3–C6	1.254(4)	C7–C6^{i}	1.456(5)
C1–C2	1.438(6)		
Bond angles			
C1–N2–H6	123 (4)	C7–C6–C7^{i}	90.1 (3)
C1–N2–H7	112 (5)	C6–C7–C6^{i}	89.9 (3)
C1–N1–H1	107 (4)	C2–O1–H5	107 (4)

Symmetry code: ^{i} $2-x, 1-y, 1-z$.

Table 5. Hydrogen bonding geometry (Å, deg) for **2**.

D–H···A	D–H	H···A	D···A	D–H···A
N1–H1···O3^{i}	1.14 (7)	1.81 (7)	2.726 (5)	135 (5)
N2–H6···O2^{ii}	0.81 (5)	2.14 (6)	2.944(6)	170 (6)
N2–H7···O1	0.87(7)	2.28 (7)	2.697 (6)	110 (5)
N2–H7···O4	0.87 (7)	2.12 (7)	2.970 (6)	166 (7)
O1–H5···O2	1.43(12)	1.21 (11)	2.606 (5)	162 (9)
O4–H9···O3^{iii}	1.25 (9)	2.02 (8)	2.968 (5)	129 (5)
C5–H2···O4^{i}	1.15 (5)	2.20 (5)	3.339 (6)	169 (4)

Symmetry codes: ^{i} $1-x, y-1/2, 1/2-z$; ^{ii} $x-1, -1/2-y, z-3/2$; ^{iii} $x-1, y, z$.

C=O bond. The C1–N1 bond length [1.339(5) Å] in the pyridine ring is approximately equal to the length of a previously reported C–N double bond [30] (Table 4).

The crystal packing of **2** is again three-dimensional, constructed from van der Waals interactions and $\pi\cdots\pi$ interactions between parallel sheets held together by N–H···O and O–H···O hydrogen bonds (Table 5). Anions and cations interact through a pair of self-complimentary N–H···O bonds to form a cyclic

$R_2{}^2(9)$ ring [33] (Fig. 7). The N1···O3 [2.726(5) Å] distance is shorter than the N2···O2 [2.944(6) Å] distance, in spite of the facts that the formal positive charge resides on the $N1^+H$ group and that positively charged hydrogen bonds are expected to be stronger [17].

Experimental Section

Materials and measurements

All chemicals used were analytical reagent products. The IR spectra were recorded in the 4000 – 400 cm^{-1} region with a Mattson 1000 FT-IR spectrometer using KBr pellets. A Perkin Elmer Diamond TG/DTA thermal analyzer was used to record simultaneously TG, DTG and DTA curves in static air atmosphere at a heating rate of 10 K min^{-1} in the temperature range 20 – 700 °C using platinum crucibles.

Preparation of the squarate salts

Squaric acid (456 mg, 4 mmol) and 2-hydroxyaniline (873 mg, 8 mmol) or 2-amino-3-hydroxypyridine (881 mg, 8 mmol) were dissolved in a water/methanol (20 mL) mixture (1 : 1) and the solutions were heated to 50 °C in a temperature-controlled bath and stirred for 1 h. The reaction mixtures were then slowly cooled to r. t. The crystals formed were filtered and washed with 10 mL of water and methanol and dried in *air*. Calcd. for $C_{16}H_{16}N_2O_6$ (**1**): C 57.83, H 4.85, N 8.43; found C 57.80, H 4.85, N 8.44. Calcd. for $C_{14}H_{18}N_4O_8$ (**2**): C 45.41, H 4.90, N 15.13; found C 45.44, H 4.84, N 15.21.

Crystallographic analyses

Data collections were performed on a STOE IPDS II image plate detector using MoK_α radiation (λ = 0.71073 Å). Intensity data were collected at 296 K. Data collection and cell refinement: X-AREA [34]. Data reduction and absorption correction by integration: X-RED [34]. The structures were solved by Direct Methods using SIR97 [35], and anisotropic displacement parameters were applied to non-hydrogen atoms in a full-matrix least-squares refinement based on F^2 using SHELXL-97 [36]. Molecular drawings were obtained using ORTEP-III [37].

Supplementary material

CCDC 605867 and 605868 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

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