The solid state structure of pyridinium hydrogen squarate

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Barbara Modec

Department of Chemistry and Chemical Technology, University of Ljubljana, Večna pot 113, 1000 Ljubljana, Slovenia

ABSTRACT

The solvothermal reaction of $(PyH)[MoOBr_4]$ (PyH^+ = pyridinium cation, $C_5H_5NH^+$) with squaric acid (H_2Sq = 3,4-dihydroxy-3-cyclobutene-1,2-dione, $H_2C_4O_4$) in pyridine has inadvertently afforded apart from a dinuclear molybdenum(V) complex with a coordinated squarato dianion another product, a simple pyridinium salt of hydrogen squarate, $(PyH)(HSq)$ (HSq^- = hydrogen squarate, $HC_4O_4^-$). The salt crystallizes in the monoclinic space group $P\,2_1/c$ with $a = 10.1061(9)$ Å, $b = 11.0436(10)$ Å, $c = 7.4497(7)$ Å and $\beta = 103.188(2)°$. Its solid state structure consists of infinite chains made of HSq^- ions linked *via* strong $O-H \cdots O^-$ hydrogen bonds. The corresponding $O \cdots O$ contacts are 2.5604(13) Å. The counter-cations, protonated pyridine molecules, are attached to these chains *via* $N^+-H \cdots O^-$ hydrogen bonds. The X-ray structure analysis has revealed stacking arrangements of both ions with short interplanar spacings. Weak intermolecular interactions of the $\pi \cdots \pi$ type between ions of the same charge and of the $C-H \cdots O$ type between the oppositely charged ions were shown to play an important role in their packing.

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## 1. Introduction

Squaric acid (H_2sq), 3,4-dihydroxy-3-cyclobutene-1,2-dione, is one of the most studied representatives of oxocarbon acids. Oxocarbon species which include besides a squarate dianion ($C_4O_4^{2-}$) also deltate ($C_3O_3^{2-}$), croconate ($C_5O_5^{2-}$) and rhodizonate ($C_6O_6^{2-}$) have symmetric π-systems with oxygen atoms involved in delocalization [1]. The structural formula of squaric acid is depicted in Scheme 1. The acid is a very strong diprotic acid with $pK_1 = 1.2–1.7$ and $pK_2 = 3.2–3.5$ [2,3]. Through the loss of protons from one or both of the OH groups, it forms salts which contain either a hydrogen squarate anion, throughout the text denoted as HSq^-, or a squarate dianion, denoted as Sq^{2-}. The acid and both of its anions are almost perfect flat species with π-conjugation of C—C and C—O bonds. All can participate in hydrogen-bonding interactions: whereas squarate dianion can only act as a strong hydrogen bond acceptor, the parent acid and its mononeutralized form, HSq^- ion, are both potent donors and acceptors.

Recent research on the acid and its anions has been focused on their applications as active pharmaceutical ingredients [4–6], or fluorescent biomarkers with large second- and third-order nonlinear optical responses [7,8]. Their application in crystal engineering has also been reported [9,10]. Our interest in squarate ions

is due to their bridging function in multinuclear transition metal complexes. For instance, $[Mo_2O_4(Py)_4(Sq)]$ and $[Mo_4O_8(Sq)_4]^{4-}$, a pair of molybdenum(V) complexes containing a metal–metal bonded $\{Mo^V_2O_4\}^{2+}$ structural unit which were synthesized in our laboratory, contain squarato ligands engaged in a μ_2-1,2-bis(monodentate) coordination manner to a pair of metal atoms spanning either a short distance of *ca.* 2.5 Å or a significantly longer one, *ca.* 3.4 Å [11]. In the latter case, the metal ions bridged by the squarate belong to two different $\{Mo^V_2O_4\}^{2+}$ cores. One of the reactions produced apart from the anticipated metal complex a colourless crystalline material. The lack of colour spoke in favour either of the oxidation of metal to VI state or the formation of a simple salt of squaric acid [12]. Herein, a solid state structure of this product, pyridinium hydrogen squarate, is reported and compared with the structures of related compounds. Surprisingly, although a search on the CSD [13] has disclosed numerous structures of salts with the hydrogen squarate ion, it has shown no entry for the title compound. A variety of hydrogen-bonding patterns displayed by the monoanion can be classified into four basic groups. With the details of each being already presented in two reviews [10,14], only brief descriptions will be given. The solid state structures of the HSq^- compounds contain either isolated ions or two, four or an infinite number of ions linked *via* strong $O-H \cdots O$ hydrogen bonds [15]. The majority of structures is dominated by a centrosymmetric $(HSq^-)_2$ dimer which bears a strong resemblance to the dimer encountered among the structures of carboxylic acids [16].
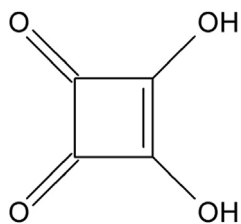
Scheme 1. The structural formula of squaric acid, H_2Sq.

Whereas the assembly of four ions to produce a cyclic tetramer finds only a rare occurrence, the *catena* synthon represents the other principal arrangement of HSq^- ions. Depending on the relative positions of the OH and O functions within the ion, two types of chains can be distinguished, 1,2-chains (known also as α-chains) and 1,3-chains (β-chains). In 1,2-chains, the hydrogen bond acceptor is the O function which is in a vicinal position to OH. In 1,3-chains, the acceptor is positioned diagonally opposite to the hydroxyl moiety.

2. Experimental

2.1. Preparation of pyridinium hydrogen squarate

A mixture of $(PyH)[MoOBr_4]$ (120 mg, 0.235 mmol), squaric acid (114 mg, 1.00 mmol) and pyridine (4 mL) was placed in a glass tube which was sealed and heated for 120 h in an electric oven maintained at 115 °C. The reaction vessel was allowed to cool slowly to room temperature. The vessel contained an orange solution and two solid phases: orange crystals of $[Mo_2O_4(Py)_4(Sq)]\cdot 2Py$ and colourless crystals of $(PyH)(HSq)$ [11].

2.2. X-ray crystallography

The crystal was mounted on the tip of a glass fibre with a small amount of silicon grease and transferred to a goniometer head. Crystallographic data were collected on a Bruker P4 diffractometer equipped with an SMART CCD system. Data processing was accomplished with the SAINT program [17]. Absorption correction was made using SADABS [18]. The coordinates of all non-hydrogen atoms were found *via* direct methods using the structure solution programme SHELXS [19]. All hydrogen atoms with the exception of H1n (on N1) and H1o (on O1) were placed at calculated positions (C–H = 0.93 Å) and were allowed to ride on their parent atoms. Hydrogen atoms H1n and H1o were located by means of a combination of least-squares refinement and difference Fourier maps in the SHELXL 97 programme [19] and were refined with isotropic displacement parameters. Figures depicting the structures were prepared by ORTEP [20] and Mercury [21]. Cell parameters and refinement results are summarized in Table 1.

3. Results and discussion

The crystal structure of $(PyH)(HSq)$ consists of hydrogen squarate anions and protonated pyridine molecules as countercations. The compound crystallizes in a monoclinic space group $P\,2_1/c$ with both ions residing on general positions. Their ORTEP drawings are shown in Fig. 1, and an exhaustive list of the geometric parameters of the HSq^- ion is given in Table 2. The HSq^- ion is nearly planar with maximum deviation of its atoms from the best plane of four carbon atoms being 0.043(2) Å. It displays two short C–O bonds, *i.e.*, C3–O3 = 1.2155(15) and C4–O4 = 1.2233(15) Å, one intermediate $[C2-O2 = 1.2741(14)$ Å$]$ and one long C–O bond

Table 1
Crystal data for (PyH)(HSq).

Empirical formula	$C_9H_7NO_4$
Formula mass	193.16
Crystal system	monoclinic
Space group	$P\,2_1/c$
a, Å	10.1061(9)
b, Å	11.0436(10)
c, Å	7.4497(7)
α, deg	90
β, deg	103.188(2)
γ, deg	90
V, Å^3	809.52(13)
Z	4
d_{calc}, g cm^{-3}	1.585
μ, mm^{-1}	0.127
λ, Å	0.71073
Temperature, K	92(2)
Collected reflections	10371
Unique reflections, R_{int}	2761, 0.0384
Observed reflections	2057
$R1^a$ $[I > 2\sigma(I)]$	0.0512
$wR2^b$ [all data]	0.1267

^{a} $R1 = \sum||F_o|-|F_c||/\sum|F_o|$.
^{b} $wR2 = \{\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.
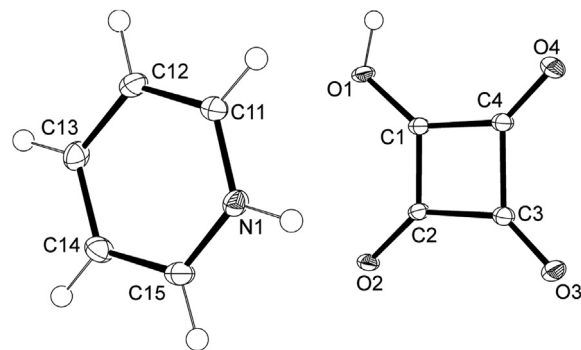

Fig. 1. ORTEP drawings of the constituent ions in pyridinium hydrogen squarate with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are drawn at arbitrary size.

Table 2
Bonding pattern (Å, °) in (PyH)(HSq).

C1–O1	1.3119(15)	C1–C2	1.4139(17)
O1–H1o	0.94(2)	C1–C4	1.4505(17)
C2–O2	1.2741(14)	C2–C3	1.4905(18)
C3–O3	1.2155(15)	C3–C4	1.5193(18)
C4–O4	1.2233(15)		
C1–C4–C3	87.89(9)	O2–C2–C1	134.46(12)
C4–C3–C2	87.96(9)	O2–C2–C3	135.14(11)
C3–C2–C1	90.40(10)	O3–C3–C2	136.39(12)
C2–C1–C4	93.71(10)	O3–C3–C4	135.64(12)
O1–C1–C4	136.01(11)	O4–C4–C3	135.45(11)
O1–C1–C2	130.28(11)	O4–C4–C1	136.66(12)

$[C1-O1 = 1.3119(15)$ Å$]$. Both short bonds have values which are close to a C=O double bond. The C1–O1 bond length confirms the presence of proton on O1 atom, whereas the C2–O2 bond length confirms the presence of negative charge on O2 atom. The C–C bond length at the carbon atoms carrying the OH and the O$^-$ groups is shorter than the remaining three C–C bond lengths, *i.e.*, C1–C2 = 1.4139(17) Å *vs.* C1–C4 = 1.4505(17), C2–C3 = 1.4905(17) and C3–C4 = 1.5193(18) Å. Such a distribution of C–C bond lengths speaks of a localized C=C double bond between C1 and C2 atoms. The C–C–C angles within the HSq^- ion deviate significantly from