Bulgarian Chemical Communications, Volume 50, Special Issue J (pp. 123–129) 2018

Crystal structure and spectral study of 3-methylpyridazinium hydrogensquarate

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Received March, 2018; Revised April, 2018

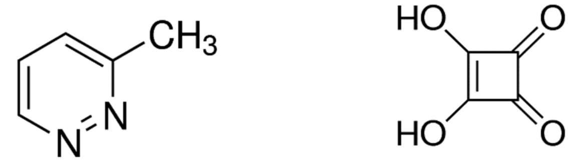
The crystal structure of 3-Methylpyridazinium hydrogensquarate was determined by single-crystal X-ray diffraction technique. The compound crystallizes in the monoclinic space group $P2_1/c$. The crystal packing shows the formation of layers of hydrogen squarate anions and 3-methylpyridazinium cations, connected by strong hydrogen O-H···O and N-H···O bonds. The novel derivative of squaric acid was spectroscopically characterized in solution by UV/Vis- and in solid state by means of FTIR-spectroscopy.

Key words: Single crystal X-ray diffraction, FTIR, UV/Vis.

INTRODUCTION

The diazines and the substituted azines are studied because of their important properties in biology, medicinal chemistry and fundamental chemistry of the heterocycles [1–4]. Recently the synthesis, the crystal structure and the spectroscopic properties of cyano-bridged two-dimensional coordination polymers with axially bonded 3-methylpyridazine (3-MetPy) were published by Gör *et al.* [5] with vibrational assignment of the bands from the IR and Raman spectra to the corresponding normal vibrations.

The hydrogen-bonded supramolecular patterns found in crystals of squaric acid (H_2Sq) and its anions hydrohensquarate (HSq) and squarate (Sq) were extensively studied [6–21]. The self-assembly of hydrogensquarate was studied of many researchers: Angelova [6–7], Kolev et al. [8–14] but the detailed study of crystal structure and spectral characteristics have been given by Koleva et al. [15–20]. Concerning the crystal chemistry of HSq anion [21], it was proved that it exists in different supramolecular organizations, such as chains, dimmers, tetramers, etc.. In water solution, H_2Sq has a protic behavior with formation of both anions HSq and Sq. The presented paper is dedicated to study of the ability of the squaric acid to protonate an organic base, namely 3-MetPy, and thus to form an organic salt (Scheme 1). Here, the synthesis, crystal structure and spectroscopic characteristics of a novel compound 3-methylpyridazinium hydrogensquarate have been presented and discussed in order to give an additional information about the arrangement of the HSq-anions in its solid state



3-Methylpyridazine Squaric acid

Scheme 1. Starting compounds.

EXPERIMENTAL

Synthesis

The starting compounds for the synthesis of 3-methylpyridazinium hydrogensquarate (3MPHSq), 3-methylpyridazine, $C_5H_6N_2$ and squaric acid, $C_4H_2O_4$ were purchased from Sigma Aldrich (USA). The base, 3-MetPy (2 mmol, 0.188 g) dissolved in ethanol (10 mL) was added with continuous stirring to the 45 mL aqueous solution of H_2Sq (2 mmol, 0.228 g) and then the solution obtained was stirred

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for 24 h at 40 °C. The resulting colorless crystals were filtered off, washed with ethanol, and dried on P_2O_5 at 298 K, yield 88%. The product was purified by multiple recrystallizations from distilled water. Crystals suitable for X-ray diffraction of 3MPHSq were grown by slow evaporation from double-distilled water.

Experimental methods

The IR-spectra (KBr-disks and Nujol mulls) were measured on a Thermo Nicolet 6700 FTIR-spectrometer (4000–400 cm^{-1}, 2 cm^{-1} resolution, 32 scans).

UV-spectra of solutions of the compound in ethanol (Uvasol, Merck) at concentration of 2.5×10^{-5} M were recorded at room temperature on a Thermo Scientific Evolution 300 UV-VIS-spectrophotometer (10 mm quartz cells have been used).

A colorless plate crystal of 3MPHSq with the size $0.50\times0.30\times0.12$ mm^3 was selected for data collection with a Bruker SMART X2S diffractometer using a monochromatic Mo-Kα (λ = 0.71073 Å) microfocus source with a Bruker APEX-II CCD detector at 300.15 K. APEX II software was used for data collection, cell refinement and data reduction [23]. Absorption corrections based on equivalent reflections were applied using SADABS-2008. The crystal structure was solved by direct method using SHELXS-97 [24]. All non-hydrogen atoms of the molecule were located from the electron-density map. All hydrogen atoms were placed in calculated positions. To refine the structure, the program SHELXL97 [25], version 2014/7 implemented in program OLEX2 was used [26]. Full-matrix least-squares refinement was carried out till the final refinement cycles converged to an $R = 0.0476$ and $wR(F^2) = 0.1187$ for the observed data. The OLEX software was applied to prepare the materials for publication. The crystallographic, X-ray data collection and refinement statistics for the compound are given in Table 1. Selected bond lengths and bond angles are summarized in Table 2 and hydrogen bonding interactions are given in Table 3. ORTEP diagram for the studied compound is shown on Fig. 1. CCDC 1831416 contains the supplementary crystallographic data

Table 1. Crystal data and structure refinement for 3MPHSq

Empirical formula	$C_{18}H_{16}N_4O_8$
Formula weight	416.35
Temperature/K	300.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.7853(14)
b/Å	21.557(3)
c/Å	8.8921(13)
α/°	90
β/°	90.270(5)
γ/°	90
Volume/Å^3	1875.7(4)
Z	4
ρ_{calc} g/cm^3	1.474
μ/mm^{-1}	0.118
F(000)	864.0
Crystal size/mm^3	0.5 × 0.3 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.778 to 50.086
Index ranges	$-11 \le h \le 11, -24 \le k \le 25, -10 \le l \le 10$
Reflections collected	16920
Independent reflections	3297 [$R_{int} = 0.0997$, $R_{sigma} = 0.0817$]
Data/restraints/parameters	3297/0/280
Goodness-of-fit on F^2	0.984
Final R indexes [I>=2σ (I)]	$R_1 = 0.0476$, $wR_2 = 0.1187$
Final R indexes [all data]	$R_1 = 0.0733$, $wR_2 = 0.1296$
Largest diff. peak/hole / e Å^{-3}	0.23/-0.27
CCDC number	1831416

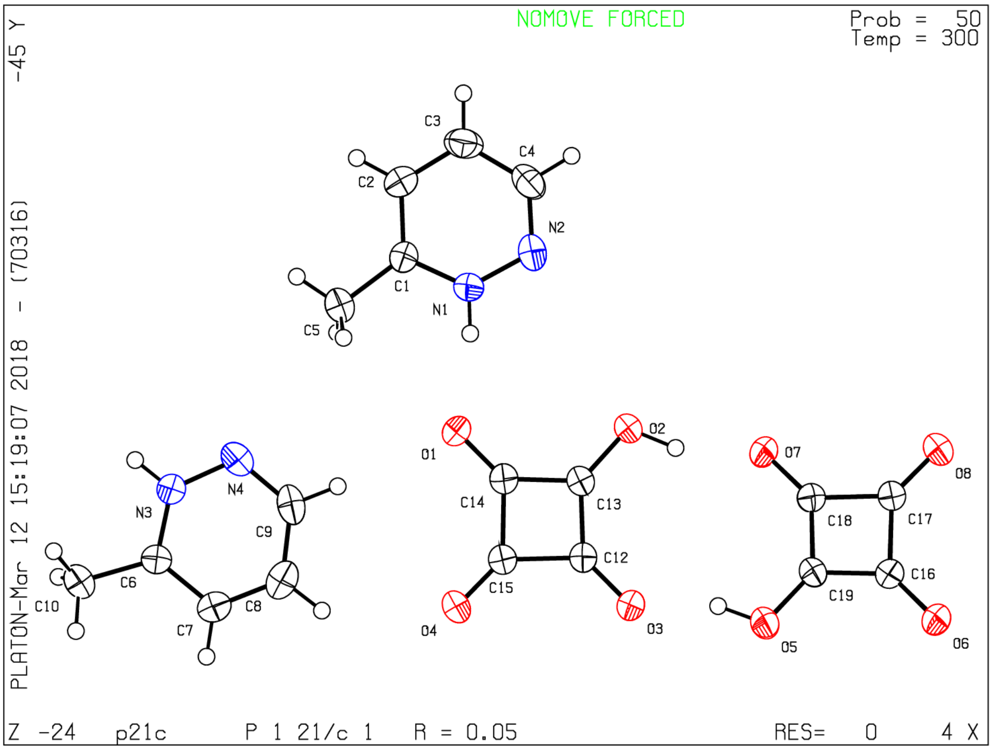

Fig. 1. Asymmetric unit of 3MPHSq. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are drawn at arbitrary size.

for the compound [27]. The drawings were prepared using Mercury version 3.3 [28].

RESULTS AND DISCUSSION

The compound 3MPHSq crystallizes in monoclinic $P2_1/c$ space group. The asymmetric unit contains two hydrogen-squarate anions and two 3-methylpyridazinium cations (Fig. 1). All molecular geometry parameters exhibit typical values [15–21]. The hydrogen-squarate ions form classical α-dimers [21], (Fig. 2) via hydrogen-bonding interactions. The observed O5-H5···O3 and O2-H2… O7 distances, respectively, 2.536 and 2.561 Å indicate strong hydrogen bond formation in the dimeric structure.

The two 3-methylpyridazine base are protonated at the N1- and N3-atoms, respectively and thus the formed pyridazinium cations (3-MetPyH) are joined to each HSq ions from the dimmer by N3-H3···O6 and N1-H1…O1 hydrogen bonds (2.676 and 2.684 Å, Tabl. 2). Thus the hydrogen bonding network leads to formation of tetramers along *a*-axis from two hydrogen-squarate ions and two side pyridazinium cations with length approximately of 1.5 nm (16.581 Å). In the crystal structure, the tetramers build finite wavy layers as the shortest distance between them is 4.488 Å. The reported structure is the first crystallographically characterized salt of 3-methylpyridazine.

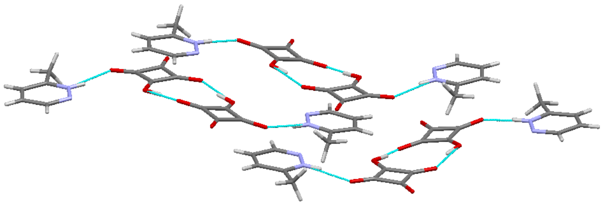

Fig. 2. Hydrogen-bonding pattern in the structure of 3MPHSq. Hydrogen bonds are represented by dashed lines.

The presence of aromatic heterocyclic six-membered rings containing two N-atoms is probably the reason for the layered structure formation. The interaction between the layers is most probably at the expense of van der Waals forces.

Infrared and UV-spectra

The experimental IR-spectrum of 3MPHSq is characterized by a broad absorption band within the 3400–2100 cm^{-1} range corresponding to overlapped

Table 2. Selected geometrical parameters for 3MPHSq (Å, °)

Bond Lengths			
O4 —C15	1.228(2)	C1—C2	1.397(3)
O2—C13	1.317(2)	C4—C3	1.398(3)
O1—C14	1.248(2)	C3—C2	1.363(3)
O3—C12	1.255(2)	C9—C8	1.402(3)
N1—N2	1.343(2)	C15—C14	1.497(3)
N1—C1	1.327(2)	C12—C13	1.421(3)
N2—C4	1.311(3)	C13—C14	1.424(3)
C5—C1	1.489(3)	C15—C12	1.496(3)
Bond Angles			
C1—N1—N2	126.76(18)	O3—C12—C1	137.1(2)
C4—N2—N1	115.46(19)	C13—C12—C15	89.50(16)
N1—C1—C5	118.42(18)	O2—C13—C12	135.99(19)
O4—C15—C12	135.7(2)	O2—C13—C14	130.50(19)
N1—C1—C2	117.0(2)	O1—C14—C15	134.2(2)
C2—C1—C5	124.60(19)	O1—C14—C13	136.5(2)
N2—C4—C3	123.5(2)	C13—C14—C15	89.35(16)
C2—C3—C4	118.2(2)	O3—C12—C15	133.35(19)
C3—C2—C1	119.1(2)	C12—C15—C14	87.63(16)
C12—C13—C14	93.51(17)	O4—C15—C14	136.6(2)

Table 3. Hydrogen Bonds and weak C–H…O interactions (Å, °) in the crystal structure of 3MPHSq

D—H···A	d(D-H)	d(H-A)	d(D-A)	D-H-A
O2—H2A···O7^{1}	0.95(3)	1.65(3)	2.561(2)	159(2)
O5—H5···O3^{2}	0.94(3)	1.63(3)	2.536(2)	160(2)
N1—H1···O1^{3}	0.86	1.84	2.684(2)	168.5
N3—H3A···O6	0.86	1.83	2.676(2)	169.0
C4—H4···O6	0.93	2.47	3.396(3)	172.4
C2—H2···O3^{5}	0.93	2.53	3.367(3)	150.4
C9—H9···O1^{6}	0.93	2.43	3.361(3)	176.3
C7—H7···O7^{7}	0.93	2.53	3.387(3)	152.9

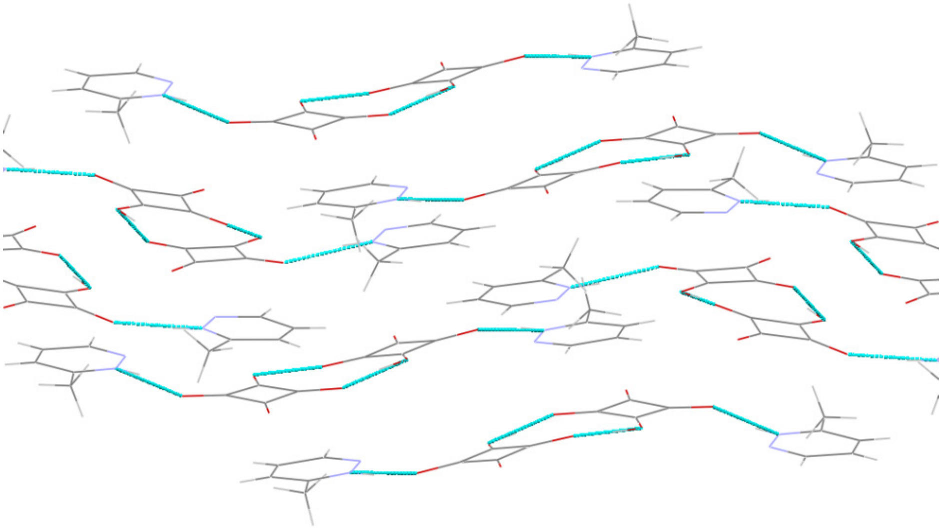

Fig. 3. O–H···O and N–H···O bonded layers in the structure of 3MPHSq.

$\nu_{OH(Sq)}$ and $\nu_{N^{+}H(3\text{-}MetPyH)}$ stretching vibrations. The series of bands within the 3100–3000 cm^{-1} and 2965 and 2800 cm^{-1} regions correspond to the stretching vibration $\nu_{3MetPyCH}$ and $\nu_{(CH_3)}$ modes. The bands in the interval 1810–1590 cm^{-1} belong to $\nu^{s}_{C=O(Sq)}$, $\nu^{as}_{C=O(Sq)}$ and $\nu_{C=C(Sq)}$ stretching vibrations of the hydrogensquarate anion. The bands at 1644 cm^{-1} and 1605 cm^{-1} can be attributed to $\nu_{N^{+}H}$ bending vibrations as the bands at 1545 and 1385 cm^{-1} could be assigned to $\nu^{as,s}(COO^{-})$ of the one-deprotonated carboxylic group.

The observed shift of the bands belonging to NH^{+} (base), -C=O (HSq) and COO^{-} (HSq) in respect to the free acid and base (Fig. 4, Table 4) prove the participation of the groups in hydrogen-bond formation. The assignments of the bands are in accordance with theoretical data published in [15, 22].

The molecular structure in solution was studied by ultraviolet absorption spectroscopy, which in general is regarded as very useful to study the chemical behavior and the electronic orientation of the substituents in heteroaromatic molecules [29]. The base 3-MetPy shows the characteristic π→π* at 263 (lgε=4.5) and n→π* at 315 nm (lgε = 4.0) (Fig. 5).

In the spectrum of the studied compound 3-MetPySq, only the band for π→π* band (lgε =

Table 4. Assignment of the experimental IR- bands 3MPHSq

Assignment	IR bands of 3MPHSQ [cm^{-1}]
νCH	3057
νOH_{Sq}	2730
νOH_{Sq}	2651
νOH_{Sq}	2572
νOH_{Sq}	2504
νOH_{Sq}	2159
νOH_{Sq}	2082
$\nu^{s}(C{=}O)_{Sq}$	1805
$\nu^{as}(C{=}O)_{Sq}$	1663
8a + νSq	1644
19a; 19b	1538
$\nu(C{=}C)_{Sq})$	1596
$\nu(C—O^{-})_{Sq}$	1542
$\nu(C—C)_{Sq}$	1470
$\nu C—CH_3$	1250
$\nu(C—C)_{Sq}$	1169
$\nu(C—C)_{Sq}$	1142
$\nu(C—C)_{Sq}$	1095
$r(CH_3)$	1049
δCH(ring)	1020

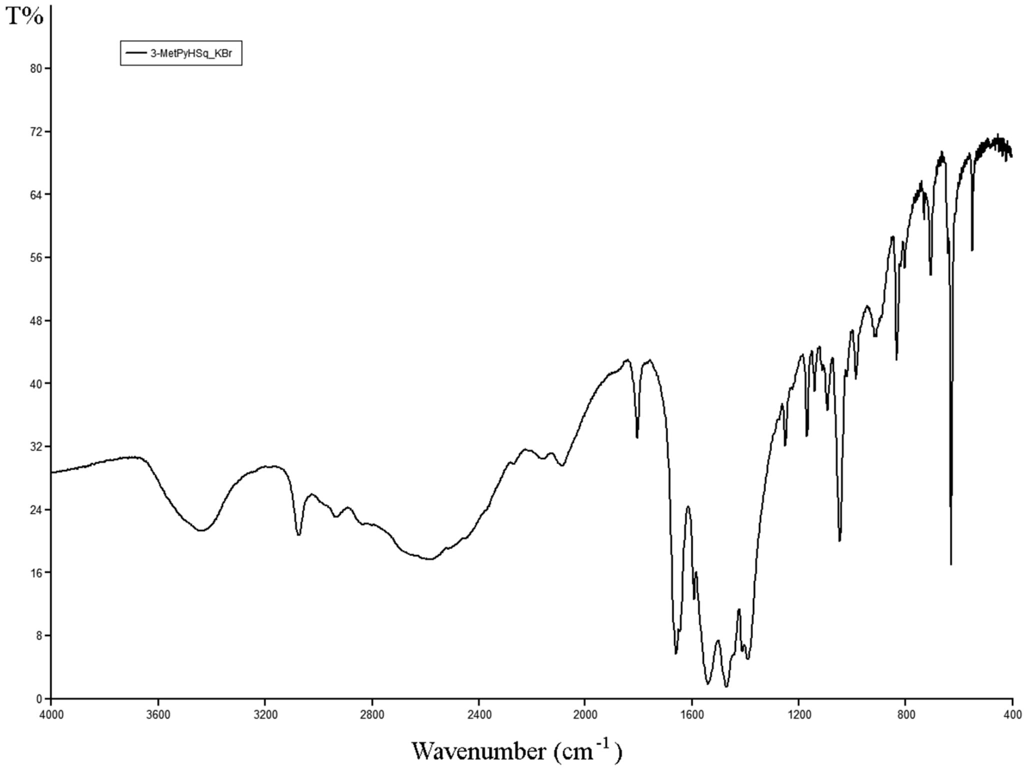

Fig. 4. FTIR-spectrum of 3-Methylpyridazinium hydrogensquarate – KBr pellet.

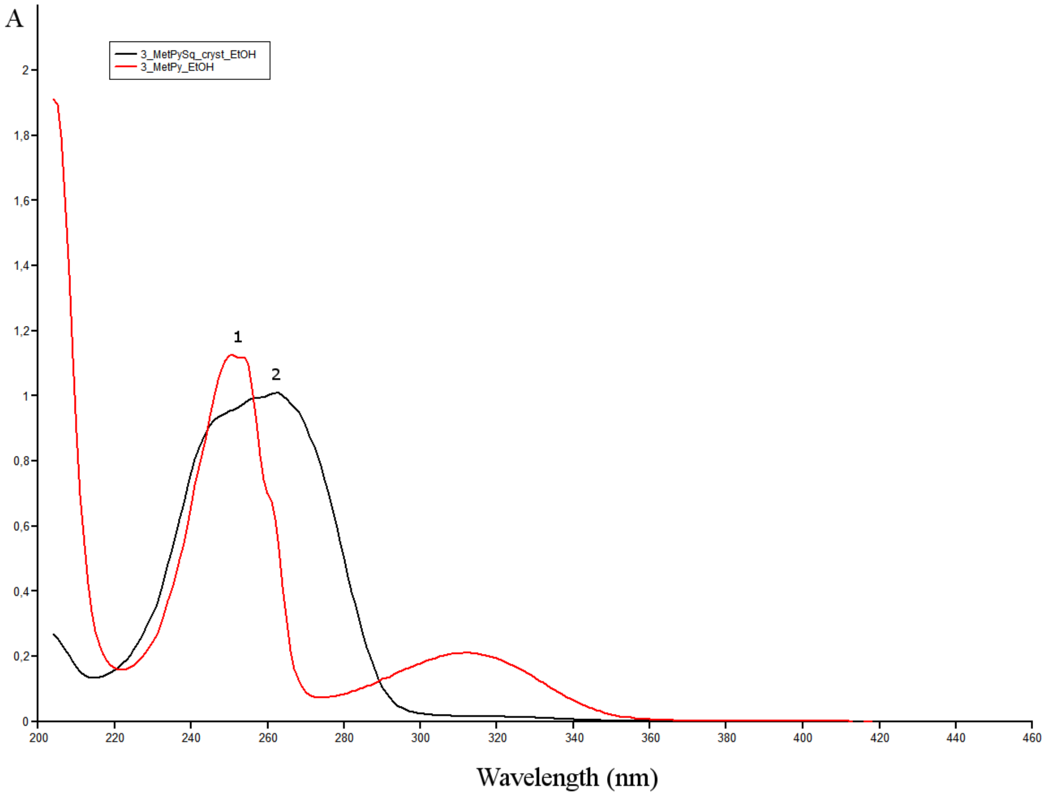

Fig. 5. UV-spectra of 3-Methylpyridazine (1) and 3-Methylpyridazinium hydrogensquarate (2) dissolved in ethanol at concentration 2.5.10-5 molL-1.

4.8) was observed. As a consequence of the protonation of one of the nitrogen atoms (Fig. 5), a hypsochromic shift of the n→π* band leads to overlay with the more intensive π→π* band.

CONCLUSION

The new compound 3-methylpyrdazinium hydrogensquarate has been synthesized, isolated, spectroscopically and structurally characterized, using single crystal X-ray diffraction, IR spectroscopy and UV-spectroscopy. The effects of N-protonation on the optical properties are elucidated by the comparison of the data of the protonated and neutral compound. The compound crystallizes in the monoclinic $P2_1/c$ space system and the structure consists of infinite layers. The hydrogensquarate ions form stable α-dimers via inter anion hydrogen-bonding interactions. The observed O5-H5···O3 and O2-H2···O7 distances, respectively, 2.536 and 2.561 Å indicate strong hydrogen bond formation in the dimeric structure. We reported for the first time the structural motif of α-dimer with formation of hydrogen bonds with different distances (2.536 and 2.561 Å).

REFERENCES

1. D. Mantu, M. C. Luca, C. Moldoveanu, G. Zbancioc, I. I. Mangalagiu, *Eur. J. Med. Chem.*, **45**, 5164 (2010).
2. R. M. Butnariu, I. I. Mangalagiu, *Med. Chem.*, **17**, 2823 (2009).
3. C. Moldoveanu, G. Mangalagiu, G. Drochioiu, M. Caprosu, M. Petrovanu, I. Mangalagiu, New Potential Anti-tuberculosis Compounds Derived from Diazine, in: Al. I. Cuza (Ed.), An. St. Univ., 2003.
4. A. M. Zbancioc, G. Zbancioc, C. Tanase, A. Miron, C. Ursu, I. I. Mangalagiu, *Lett. Drug Des. Discov.*, **7**, 644 (2010).
5. K. Gör, G. Kürkçüoğlu, O. Yeşilel, O. Büyükgüngörd, *Inorg. Chim. Acta*, **414,** 15 (2014).
6. O. Angelova, R. Petrova, V. Radomirska, T. Kolev, *Acta Cryst. C*, **52**, 2218 (1996).
7. O. Angelova, V. Velikova, T. Kolev, V. Radomirska, *Acta Cryst. C*, **52**, 3252 (1996).
8. T. Kolev, Z. Glavcheva, R. Stahl, H. Preut, P. Bleckmann, V. Radomirska, *Acta Cryst. C*, **53**, IUC9700010 (1997).
9. T. Kolev, H. Preut, P. Bleckmann, V. Radomirska, *Acta Cryst. C*, **53**, 805 (1997).
10. T. Kolev, H. Preut, P. Bleckmann, V. Radomirska, *Z. Kristallogr. – New Cryst. Struct.*, **212**, 414 (1997).

11. T. Kolev, R. Stahl, H. Preut, P. Bleckmann, V. Radomirska, *Z. Kristallogr. – New Cryst. Struct.*, **212**, 415 (1997).
12. T. Kolev, R. Stahl, H. Preut, V. Koniczek, P. Bleckmann, V. Radomirska, *Z. Kristallogr. – New Cryst. Struct.*, **212**, 417 (1997).
13. T. Kolev, R. Stahl, H. Preut, V. Koniczek, P. Bleckmann, V. Radomirska, *Z. Kristallogr. – New Cryst. Struct*., **213** (1), 167 (1998).
14. T. Kolev, R. Stahl, H. Preut, P. Bleckmann, V. Radomirska, *Z. Kristallogr. – New Cryst. Struct*., **213** (1), 169 (1998).
15. B. B. Koleva, T. Kolev, R. W. Seidel, M. Spiteller, H. Mayer-Figge, W. S. Sheldrick, *J. Phys. Chem. A*, **113**, 3088 (2009)
16. B. B. Koleva, T. Kolev, R. W. Seidel, Ts. Tsanev, H. Mayer-Figge, M. Spiteller, W. S. Sheldrick, *Spectrochim. Acta, Part A*, **71**, 695 (2008).
17. B. B. Koleva, T. Tsanev, T. Kolev, H. Mayer-Figge, W. S. Sheldrick, *Acta Cryst. E*, **63**, o3356 (2007).
18. T. Kolev, B. Koleva, R. Sedel, M. Spitreller, W. Sheldrick, *Acta Cryst. E*, **63**, o4852 (2007).
19. T. Kolev, B. Koleva, M. Spitreller, *Amino Acids*, **33**, 719 (2007).
20. T. Kolev, B. Koleva, M. Spiteller, *J. Mol. Struct.*, **877**, 79 (2008).
21. G. Gilli, V. Bertolasi, P. Gilli, V. Ferretti, *Acta Cryst. B*, **57**, 859 (2001).
22. T. Kolev, T. Pajpanova, T. Dzimbova, S. Zareva, M. Spiteller, *J. Mol. Struct.*, **1102**, 235 (2015).
23. Bruker (2012). SADABS. Bruker AXS Inc., Madison, Wisconsin, USA; Bruker (2013). APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
24. G. M. Sheldrick, *Acta Cryst. A*, **64**, 112 (2008).
25. G. M. Sheldrick, *Acta Cryst*., *C* **71**, 3 (2015).
26. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. Howard, H. Puschmann, *J. Appl. Cryst*., **42**, 339 (2009).
27. The crystallographic data for 3MPHSq were deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 1831416. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; tel: +441223762910; fax: +441223336033; e-mail: deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk/deposit.
28. C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidock, L. Rodriguez-Monge, R. Taylor, J. Van de Streek, P. A. Wood, *J. Appl. Crystallogr*., **41**, 466 (2008).
29. F. Peral, E. Gallego, *Spectrochim. Acta Part A*, **59**, 1223 (2003).

КРИСТАЛНА СТРУКТУРА И СПЕКТРАЛНИ ХАРАКТЕРИСТИКИ НА 3-МЕТИЛПИРИДАЗИНИЕВ ХИДРОГЕНСКВАРАТ

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Постъпила март, 2018 г.; приета април, 2018 г.

(Резюме)

Кристалната структура на 3-метилпиридазиниевия хидрогенскварат беше определена посредством монокристална рентгенова дифракция. Изследваното съединение кристализира в моноклинна пространствена група $P2_1/c$, като формира слоеве от хидрогенскваратни аниони и 3-метилпиридазиниеви катиони, свързани със здрави водородни O−H···O и N−H···O връзки. Новополученото съединение е охарактеризирано в разтвор и в твърдо състояние съответно чрез УВ- и ИЧ-спектроскопия.