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On 2:1 melamine – Squaric acid dihydrate complex: The structure and vibrational spectra

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ABSTRACT

In the present paper we would like to describe the structural and dynamical properties of crystalline dihydrated complex of melamine (2,4,6–triamino-1,3,5–triazin-1-ium) with squaric acid (3,4-dihydroxycyclobut-3-ene-1,2-dione) abbreviated as MH·SQ. The X-ray diffraction studies show the presence of deprotonated units $(C_4O_4)^{2-}$ and single protonated melamine cations surrounded by tetrameric water assemblies $(H_2O)_4$. The formation of the water tetramers deserves a special attention. IR absorption and Raman spectra reflect a richness of structural units and numerous hydrogen bonds. The presence of the continua in the IR spectra, with a characteristic presence of the Hadži's trio enriched by a numerous submaxima, may be ascribed to the structural units and to the various types of hydrogen bonds. The density functional theory calculation with the periodic boundary conditions was use to precise analysis of experimental data.

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1. Introduction

Melamine – [2,4,6–triamino–1,3,5–triazine] belongs to the interesting systems from the biological viewpoint and possible applications in the field of vibrational spectroscopy. The structure of melamine was reported by Hughes [1]. The phase transitions in the pure melamine under high temperatures were observed at in-situ synchrotron X-ray study [2]. The X-ray diffraction crystal structure of melamine under high pressure was analyzed as well [3]. The binding energy of the C1s and N1s in melamine has been determined on the basis of the XPS (X-ray Photoelectron Spectroscopy) results [4]. Spectroscopic properties of melamine by the use of infrared, Raman and surface-enhanced Raman scattering (SERS) methods are presented by Mircescu et al. [5].

Computational simulations of supramolecular hydrogen-bonded aggregates of cyanuric acid-melamine rosette motifs are systems of great importance in the study of molecular self-assembly and noncovalent synthesis and particularly in designing novel aggregates with the prediction of their stabilities [6]. A design strategy in which the H-bonding allows the combination of the π-stacking tendency of melamine and the lateral interaction capability of V-shaping molecules should be noted [7]. Complexes formed by a melamine core and three V-shaped acids present a supramolecular organization of columnar assemblies with photo-tunable chirality [8]. Infinite water chains trapped in an organic framework constructed from melamine with 1,5-naphtalene-disulfonic acid via hydrogen bonds were reported [9]. The formation of the supramolecular 1:1, 1:2 and 1:3 complexes of melamine with imides is also described in literature [10]. The novel supramolecular organizations on complexes of melamine with 4,4'-bipyridyl and $AgNO_3$ are presented [11].

It has been found that melamine in its protonated form can be triggered by oxoanions to form superstructures and gelate a large amount of water [12]. Melamine-based mono carboxylate salts of aliphatic dicarboxylic acids were synthesized and characterized for gelation behavior in various solvents [13]. A co-assembled light-harvesting hydrogel of melamine with riboflavin was used to produce a white-light-emitting hydrogel by mixing with rhodamine [14,15]. A new and quick detection method for the trace of melamine in aqueous media is reported [16].

The structural analysis of the melaminium polyphosphate based on the X-ray powder diffraction and solid-state NMR data is

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reported [17]. The crystal structure study of melamine with phosphorous acid [18] as well as molecular complexes of melamine with hydroxy and dihydroxy benzoic acids are presented [19].

Vibrational FT-IR, FT-IR/ATR and Raman spectra of 3,4,9,10-perylene-tetracarboxylic diimide and melamine molecules were assigned [20]. Tetrakis (2,4,6)-1,3,5 triazinium bis (selenate) trihydrate was chosen to be studied as the potential SHG (Second Harmonic Generating) crystals for the non-linear optics [21].

The aim of our studies presented in this paper is a careful analysis of packing and vibrational features of the 2:1 melamine – squaric acid dihydrate complex components. Both elements of the complex, i.e. melamine and squaric acid evoke independently great interest due to their symmetry and proton donor and acceptor ability. In this paper investigations of crystal structure, dynamical properties (IR and Raman scattering) as well as application of the DFT calculation with the periodic boundary conditions for an experimental data analysis are presented.

2. Experimental and calculations

2.1. Synthesis of 2:1 melamine – squaric acid dihidrate complex

The 2:1 melamine – squaric acid dihydrate complex (MH·SQ) was prepared with corresponding stoichiometry. To the aqueous solution of melamine the aqueous solution of squaric acid was added. The mixed solutions were heated at boiling temperature during about 1 h. After cooling the formed crystals were filtered under vacuum and then recrystallized from the 1:4 mixture of water and methanol.

2.2. X-ray measurement

The X-ray diffraction studies were performed on an Oxford Diffraction XCalibur PX four circle diffractometer equipped with Oxford Cryosystem cooler using graphite monochromated CuK_α radiation. During the refinement an extinction and absorption correction were applied. The structure was solved by direct methods (SHELXS-97) and refined on F^2 by the full-matrix least-squares approaching the SHELXL-97 program [22]. Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were located from difference map and refined. The crystal data and structure refinement are summarized in Table 1. The structural data have been deposited at the Cambridge Crystallographic Data Centre (CCDC 1474234). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

Table 1
Crystal data and structure refinement of the complex melamine – squaric acid dihydrate (MH·SQ).

Identification code	MH·SQ
Formula	$C_{10}H_{22}N_{12}O_8$
Formula weight	438.40
T, K	100 (2)
Crystal system	Triclinic
Space group	Pī
a (Å)	3.601 (1)
b (Å)	11.133 (4)
c (Å)	11.402 (4)
α (°)	78.73 (5)
β (°)	83.55 (5)
γ (°)	67.242
V (Å^3)	441.3 (2)
Z	1
Crystal size (mm)	0.33 × 0.05 × 0.05
θ Range (°)	3.97 to 68.0
D_{calc} (g cm^{-3})	1.649
Index ranges	$-4 \le h \le 4$ $-13 \le k \le 14$ $-14 \le l \le 13$
μ(Cu K_α) (mm^{-1})	1.228
T_{min}, T_{max}	0.6879, 0.9411
No. of reflections collected	2963
No. of independent reflections	1811 (R_{int} = 0.038)
Goodness-of-fit on F^2	1.100
Final R_1, wR_2 indices [F > 4σ(F)]	0.0408, 0.1246
Final R_1, wR_2 indices (all data)	0.0463, 0.1280
$\Delta\rho_{max,\ min}$ (e Å^{-3})	0.34/−0.37

2.3. FT-IR and Raman measurements

The FT-IR spectra of the investigated complex were recorded as Nujol/Fluorolube mulls. The spectra were taken with an IFS 113v FT-IR Spectrophotometer (Bruker, Karlsruhe) equipped with a DTGS detector; resolution 2 cm^{-1}, NSS = 64. The Happ-Genzel apodization function was used. The Raman spectra of powder samples were recorded on a Nicolet Magma 860FT Raman Spectrometer. A diode-pumped Nd:YAG laser was used as the excitation source, with a power of ca. 200 mW. The back scattering geometry was applied.

Table 2
Experimental and calculated bond lengths (Å) and angles (°) for melamine squaric acid dihydrate.

Coordinates	Experimental X-ray	Calculated CASTEP/PBE
Bond lengths		
N1–C2	1.367 (2)	1.377
C2–N4	1.319 (2)	1.336
C2–N2	1.332 (2)	1.344
N2–C4	1.356 (2)	1.366
C4–N5	1.327 (2)	1.343
C4–N3	1.353 (2)	1.361
N3–C6	1.326 (2)	1.342
C6–N6	1.322 (2)	1.331
C6–N1	1.367 (2)	1.378
C11–C12	1.462 (2)	1.475
C11–C12′	1.468 (2)	1.475
C11–O1	1.258 (2)	1.261
C12–O2	1.259 (2)	1.260
N1–H1···O1	2.665 (2)	2.672
N4–H2···O2	2.846 (2)	2.860
N4–H3···N2	2.991 (2)	2.979
N5–H5···O1W	2.939 (2)	2.896
N6–H6···O1W	2.799 (2)	2.784
N6–H7···N3	2.979 (2)	2.920
O1W–H8···O2W	2.794 (2)	2.758
O2W–H9···O1	2.835 (2)	2.753
O2W–H10···O2	2.780 (2)	2.754
O1W–H11···O2W	2.794 (2)	2.758
Bond angles		
N1–C2–N2	121.5 (1)	121.2
N1–C2–N4	117.9 (1)	118.1
N2–C2–N4	120.6 (1)	120.7
C2–N2–C4	115.9 (1)	116.2
N2–C4–N3	125.8 (1)	125.5
N2–C4–N5	117.1 (1)	117.4
N3–C4–N5	117.1 (1)	117.1
C4–N3–C6	115.8 (1)	116.3
N3–C6–N1	122.0 (1)	121.3
N3–C6–N6	120.5 (1)	120.3
N1–C6–N6	117.5 (1)	118.5
O1–C11–C12	135.3 (1)	135.2
O1–C11–C12′	134.5 (1)	134.2
C12–C11–C12′	90.2 (1)	90.3
O2–C12–C11	134.9 (1)	135.1
O2–C12–C11′	135.3 (1)	135.0
C11–C12–C11′	89.8 (1)	89.7

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