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Crystal structure and spectroscopic properties of the complex of trigonelline hydrate with *p*-hydroxybenzoic acid

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ABSTRACT

The crystal structure of the 1:1:1 complex of trigonelline (N-methyl-3-carboxypyridinium, TRG) water and *p*-hydroxybenzoic acid, HBA, has been determined by X-ray diffraction. The crystals are monoclinic, space group $P2_1/c$. The carboxylic group of HBA is linked to the carboxylate group of TRG by the COOH···OOC hydrogen bond of 2.632(2) Å, while the hydroxyl group interacts, as a proton-donor, with the water molecule via the O–H···O hydrogen bond of 2.639(2) Å. The water molecule plays a role of the double proton-donor to two TRG molecules by the O–H···OOC hydrogen bonds of 2.772(2) and 2.751(2) Å. This net of hydrogen bonds forms in the crystal a layer with hydrophilic internal area and hydrophobic external area. Four structures, with different order of TRG, water and HBA in the complex, have been optimized by the B3LYP/6-31G(d,p) approach. The experimental solid-state FTIR spectrum of the complex investigated have been compared with the calculated one by the B3LYP/6-31G(d,p) approach. The assignments of the ^1H and ^{13}C chemical shifts are based on the ^1H–^1H and ^1H–^{13}C, and HMBS experiments. The isotropic magnetic shielding constants, calculated by the GIAO/B3LYP/6-31G(d,p) approach, have been used to predict the ^1H and ^{13}C chemical shifts.

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1. Introduction

N-methyl-3-carboxy-pyridinium is a naturally occurring betaine (zwitterion), known as trigonelline, TRG, isolated from various plants, seeds and western rock lobster [1–5]. In TRG the charged groups are coupled via π-electrons of pyridine ring. TRG crystallizes as monohydrate [5]. TRG as a zwitterion forms 1:1 and 2:1 crystalline complexes with mineral acids, HX [6–10]. In the 1:1 complexes of TRG·HX, two types of complexes have been recognized. The first group includes complexes with HBr, HI and HNO_3, in which a proton is transferred from acid to TRG and the anion is bonded with the carboxylic group, COOH···X^- [6]. The second group comprises complexes with $HClO_4$ and HBF_4, in which two molecules of protonated TRG form a dimer, like benzoic acid, and the anion interacts exclusively electrostatically with the positively charged nitrogen atoms [7].

In this paper, we studied the interactions between TRG, water and *p*-hydroxybenzoic acid, HBA, because the complex investigated crystallizes as monohydrate. This investigation is a continuation of our previous study of hydrogen bonds in the complexes of aliphatic and aromatic betaines with HBA [11–16]. However, the complex of TRG·H_2O·HBA is the first example of a species with water molecule incorporated in the hydrogen-bond network between betaine and HBA molecules. *p*-Hydroxybenzoic acid has two different proton-donor groups, COOH ($pK_{a1} = 4.67$) and OH ($pK_{a2} = 9.37$) [17]. Both proton-donor centers of HBA can interact with the proton-acceptor COO^- group of betaine.

2. Experimental

2.1. Materials

Trigonelline monohydrate, TRG·H_2O was prepared according to the method reported previously [18]. The 1:1 complex of trigonelline with *p*-hydroxybenzoic acid, HBA, was obtained by mixing the equimolar amounts of TRG·H_2O and HBA in methanol. The precipitate was filtered off, washed with acetonitrile and recrystallized from a acetonitrile–methanol mixture (3:1), m.p. 175 °C. Analysis for $C_{14}H_{15}NO_6$: calcd.: %C, 57.33; %H, 5.16; %N, 4.78; found: %C, 57.31; %H, 5.46; %N, 4.82. The deuterated complex was prepared by threefold crystallization from CH_3OD and the excess of solvent was removed under the reduced pressure on heating, which resulted in an anhydrous deuterated sample. The anhydrous complex of TRG·HBA was prepared in the same procedure as the deuterated complex.

2.2. Measurements

The crystals for X-ray measurements were grown from acetonitrile. Diffraction measurements were carried out at ambient temperature on a Super-Nova Diffractometer, Oxford Diffraction LTD

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Table 1
Crystal data and structure refinement for the 1:1 complex of trygonelline hydrate with *p*-hydroxybenzoic acid (**1**).

Empirical formula	$C_{14}H_{15}NO_6$
Formula weight	293.27
Temperature	293(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 14.2616(2)$ Å $b = 6.78540(10)$ Å $c = 14.6836(3)$ Å $\beta = 102.902(2)°$
Volume	1385.07(4) $Å^3$
Z	4
Calculated density	1.406 g/cm^3
Absorption coefficient	0.943 mm^{-1}
$F(0\,0\,0)$	616
Crystal size	0.1 × 0.2 × 0.25 mm
θ range for data collection	3.18–75.33°
Limiting indices	$-17 \leqslant h \leqslant 17$ $-7 \leqslant k \leqslant 8$ $-17 \leqslant l \leqslant 18$
Reflections collected/unique	5191/2775 [R(int) = 0.0119]
Completeness to $\theta = 70.00$	99.1%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2775/0/250
Goodness-of-fit on F^2	1.084
Final R indices [$I > 2\sigma_I$]	$R1 = 0.0385$, $wR2 = 0.1135$
R indices (all data)	$R1 = 0.0416$, $wR2 = 0.1164$
Largest diff. peak and hole	0.355 and −0.222 e $Å^{-3}$

equipped with CCD detector, using Cu Kα radiation. Data reduction was carried out with CrystalAlisPro/ECO RED program [19]. The structure was solved with direct methods using the SHELXS-97 program [20]. All non-hydrogen atom positions were found from E-map and hydrogen atoms were found from the difference Fourier map. Parameters of non-hydrogen atoms were refined with anisotropic displacement parameters and parameters of hydrogen atoms were refined isotropically using SHELXL-97 program [21]. The final R-factor is 0.0385 for 2775 independent reflections and 250 refined parameters. The crystal data and the details of data processing are given in Table 1 and fractional atomic coordinates in Table A are given in Supplementary materials. The complete sets of structural parameters in CIF format are available from Cambridge Crystallographic Database Center, No. CCDC 784786.

FTIR spectra were measured on a Bruker IFS 66v/S instrument, with the resolution of 2 cm^{-1}. The FTIR solid state spectra were recorded in Nujol and Fluorolube suspensions using KBr plates. Each spectrum consisted of 64 scans. Raman spectrum was measured on a Brucker FRA-106/S instrument operating at the 1064 nm exciting line of a Nd:YAG laser, with the resolution of 1 cm^{-1}. The spectrum consisted of 200 scans.

NMR spectra were recorded on a Bruker Advance DRX spectrometer operating at 599.93 and 150.85 MHz for ^1H and ^{13}C, respectively. The spectra were measured in DMSO-d_6 relative to TMS as an internal standard. The 2D ^1H–^1H (COSY), ^1H–^{13}C (HETCOR) and Heteronuclear Multiple-Bond Connectivity (HMBC) spectra were obtained with the standard Bruker software.

2.3. DFT calculations

The DFT calculations were performed with the GAUSSIAN-03 program package [22]. The calculations employed the B3LYP exchange–correlation functional, which combines the hybrid exchange functional of Becke [23,24] with the gradient-correlation functional of Lee, Yang and Parr [25] and the split-valence polarized 6-31G(d,p) basis set [26]. The magnetic isotropic shielding constants were calculated with the standard GIAO/B3LYP/6-31G(d,p) (Gauge-Independent Atomic Orbital) approach with the GAUSSIAN-03 program package. The structures are reoptimized using the conductor-like screening continuum solvation model (COSMO) [27]). All the calculated IR frequencies for **2–5** are positive and confirmed that the optimized structures were in the states of minimum energies.

3. Results and discussion

3.1. Crystal structure

Trigonelline (TRG) forms a 1:1:1 crystalline complex with water and *p*-hydroxybenzoic acid (HBA). The crystals are monoclinic, space group $P2_1/c$. The numbering scheme of atoms in the TRG·H_2O·HBA crystal is shown in Fig. 1. The bond lengths are given in Table 2, while the bond and torsion angles are moved to Supplementary materials in Table B. TRG, water and HBA molecules are linked by a number of hydrogen bonds (Fig. 2, Table 3). The HBA molecule is involved in two hydrogen bonds, engaging its both proton-donor groups, COOH and OH. The carboxylic group is engaged in the O(3)–H(3)···O(2) hydrogen bond of 2.632(1) Å, which links HBA with the neighboring molecule of TRG, while the hydroxyl group interacts with water molecule by the O(5)–H(5)···OW hydrogen bond of 2.693(2) Å. The O(4) atom of HBA carboxylic group does not participate in the hydrogen-bond network but only in the weak C–H···O(4) contact (Table 3). HBA itself crystallizes in monoclinic space group $P2_1/a$ as a monohydrate [28,29]. Pairs of HBA molecules form dimers by the hydrogen bonds between

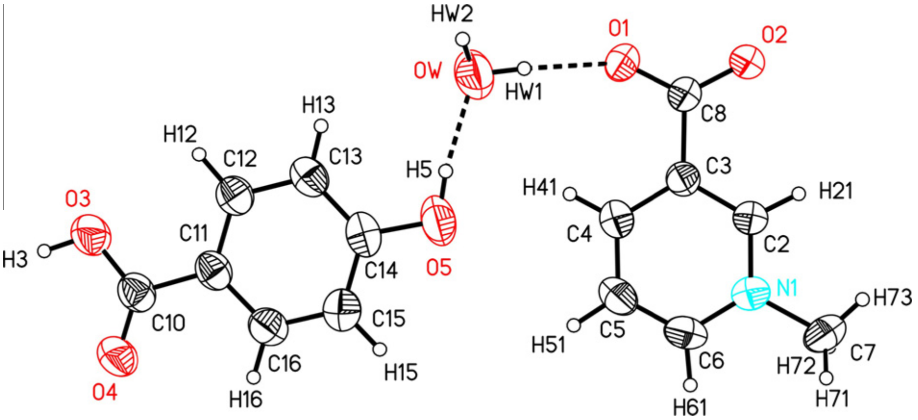

Fig. 1. Atom numbering scheme of the complex *p*-hydroxybenzoic acid–water–trigonelline (**1**).

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