Journal of Molecular Structure 1157 (2018) 247–262

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Syntheses and structure characterization of ten acid-base hybrid crystals based on imidazole derivatives and mineral acids

Kaikai Hu [a], Bowen Deng [a], Shouwen Jin [a, *], Aihua Ding [a], Shide Jin [c], Jin Zhu [a], Huan Zhang [a], Daqi Wang [b]

[a] Jiyang College, ZheJiang A&F University, Zhu'Ji 311800, PR China
[b] Department of Chemistry, Liaocheng University Liaocheng, Shandong 252059, PR China
[c] Wenhua College, Wenhuayuan Road 8, Wuchang, Wuhan, China

ARTICLE INFO

Article history:
Received 11 May 2017
Received in revised form
12 December 2017
Accepted 12 December 2017
Available online 16 December 2017

Keywords:
Structure characterization
H-bonding
Imidazole derivatives
Mineral acids

ABSTRACT

Cocrystallization of the imidazole derivatives with a series of mineral acids gave a total of ten hybrid salts with the compositions: $[(H_2bzm)(Cl)_2\cdot 3H_2O]$ **(1)**, $[(H_2bzm)(ClO_4)_2]$ **(2)**, $[(H_2bze)(Cl)_2\cdot 2H_2O]$ **(3)**, $[(H_2bze)(Br)_2\cdot 2H_2O]$ **(4)**, $[(H_2bzp)(Cl)_2\cdot 4H_2O]$ **(5)**, $[(H_2bzp)(Br)_2\cdot 4H_2O]$ **(6)**, (2-(imidazol-1-yl)-1-phenylethanone): (phosphoric acid) $[(Himpeta)^+(H_2PO_4)^-]$ **(7)**, $[(H_2impd)(Br)_2]$ **(8)**, $[(H_2impd)(ClO_4)_2]$ **(9)**, and [(Hbzml)(Cl)] **(10)**. The ten salts have been characterised by X-ray diffraction analysis, IR, and elemental analysis, and the melting points of all the salts were also reported. And their structural and supramolecular aspects are fully analyzed.

The result reveals that among the ten investigated crystals the ring N atoms of the imidazole are protonated when the acids are deprotonated, and the crystal packing is interpreted in terms of the strong charge-assisted classical H-bonds between the NH^+ and deprotonated acidic groups. Further analysis of the crystal packing of the salts indicated that a different set of additional CH—O, CH_2—O, CH—Cl, CH_2—Cl, CH—N, CH—Br, CH_2—Br, O—O, O-π, Br-π, CH-π, and π-π associations contribute to the stabilization and expansion of the total high-dimensional frameworks. For the coexistence of the various weak nonbonding interactions these structures adopted homo or hetero supramolecular synthons or both. Some classical supramolecular synthons, such as $R_2^1(7)$, $R_2^2(7)$, $R_2^2(8)$, and $R_4^2(8)$, usually observed in the organic solids, were again shown to be involved in constructing some of these H-bonding networks.

1. Introduction

The understanding of the interactions between the molecules has significantly expanded the research of molecular recognition, host-guest chemistry, crystal engineering, supramolecular chemistry, biochemistry, pharmaceutical chemistry, and materials science [1–4]. But the prediction of the crystalline structure from solely the molecular constituents is still not yet complete reliable. Crystal engineering *via* a combination of the various non-covalent interactions in creating new solids with designed structures seems to shine light on this predicament. And the noncovalent interactions such as electrostatic forces, H-bond, CH-π, π-π stacking, cation-π, anion-π, and lone pair-π contacts, as well as other weak forces have been utilized in the construction of a large number of supramolecular structures, and in the past few years, great efforts have been made to elucidate these interactions and their relationship to the final supramolecular structures [5]. Besides the noncovalent interactions, the supramolecular synthons are structural units within organic solids produced by these intermolecular interactions. And there existed two distinct categories of supramolecular synthons i.e. supramolecular homo- and heterosynthons, which was very important for the chemist to understand the synthons at the organic salt/cocrystal.

In the case of active pharmaceutical ingredients, solid organic salts with such biopharmaceutical properties as solubility, stability and hygroscopicity have been studied systematically, and these properties are relevant to the noncovalent interactions [6,7]. The acids with the donor-acceptor groups are good blocks for the multicomponent assembly [8], so they are frequently chosen as building blocks in the supramolecular crystal engineering [9].

In building acid-base hybrid crystals, the most frequently used base moieties with H-bond capability are amine, and N-heterocyclic

* Corresponding author.
E-mail address: jinsw@zafu.edu.cn (S. Jin).

https://doi.org/10.1016/j.molstruc.2017.12.041
0022-2860/

compounds [10]. Among the N-heterocyclic building blocks, the common five-membered imidazole and its derivatives have become quite popular in crystalline organic solids, due to its assembling capacity by acid-base recognition with a large number of organic and inorganic acidic molecules [11]. Among these supramolecular architectures, however, only a few reports described the crystals composed of bis(imidazole) derivatives with mineral acids [12].

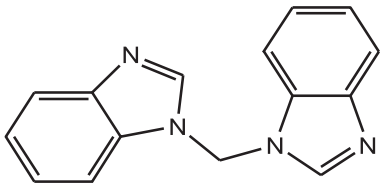
Compared with the simple imidazole, the imidazole derivatives in this text have the additional phenyl nucleus, CH_2, C=O, OH or pyridazine ring, which can generate more non-covalent bonds, thus we selected the imidazole derivatives with these units. The organic salts from the mineral acids and imidazole derivatives bis(benzimidazol-1-yl)methane (bzm), 1-(2-(1H-benzimidazol-1-yl) ethyl)-1H-benzimidazole (bze), 1-(3-(1H-benzimidazol-1-yl)propyl)-1H-benzimidazole (bzp), 2-(imidazol-1-yl)-1-phenylethanone (impeta), 3,6-bis(imidazol-1-yl)pyridazine) (impd), and 1,2-bis-benzoimidazol-1-yl-ethanol (bzmel) may tell the different H-bonds in the studied compounds.

Recently, we have focused our continuing efforts on the study of H-bonds, π-π interaction, and halogen bonds concerning N-containing derivatives [13], we will report herein the preparation and structures of ten organic salts assembled from bis(benzimidazol-1-yl)methane (bzm), 1-(2-(1H-benzimidazol-1-yl)ethyl)-1H-benzimidazole (bze), 1-(3-(1H-benzimidazol-1-yl)propyl)-1H-benzimidazole (bzp), 2-(imidazol-1-yl)-1-phenylethanone (impeta), 3,6-bis(imidazol-1-yl) pyridazine) (impd), 1,2-bis-benzoimidazol-1-yl-ethanol (bzmel), hydrochloric acid, hydrobromic acid, perchloric acid, and phosphoric acid (Scheme 1), respectively. In the present work, ten organic salts (**1**–**10**) of the protonated ligands bzm - bezel with spherical Cl^-/Br^-, and tetrahedral $ClO_4^-/H_2PO_4^-$ ions have been obtained. The ten organic salts are $[(H_2bzm)(Cl)_2\cdot 3H_2O]$ **(1)**, $[(H_2bzm)(ClO_4)_2]$ **(2)**, $[(H_2bze)(Cl)_2\cdot 2H_2O]$ **(3)**, $[(H_2bze)(Br)_2\cdot 2H_2O]$ **(4)**, $[(H_2bzp)(Cl)_2\cdot 4H_2O]$ **(5)**, $[(H_2bzp)(Br)_2\cdot 4H_2O]$ **(6)**, (2-(imidazol-1-yl)-1-phenylethanone): (phosphoric acid) $[(Himpeta)^+(H_2PO_4)^-]$ **(7)**, $[(H_2impd)(Br)_2]$ **(8)**, $[(H_2impd)(ClO_4)_2]$ **(9)**, and [(Hbzmel)(Cl)] **(10)** (Scheme 2). The synthons were listed in Scheme 1s.

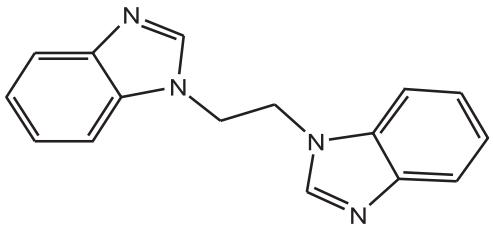
2. Experimental section

2.1. Materials and physical measurements

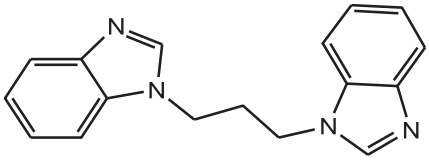
The chemicals and solvents utilized in this manuscript are analytical grade commercial products and used without purification. FT-IR spectra in range 4000–400 cm^{-1} were recorded on a Shimadzu 8400S instrument spectrometer *via* using a Golden Gate ATR accessory, and the IR bands were marked as strong (s), medium (m), and weak (w) at the preparation part. The C, H, and N data were measured micro-analytically on a Perkin-Elmer elemental analyzer with Model 2400II, and the melting points of the new salts were performed on an XT-4 thermal instrument without correction.



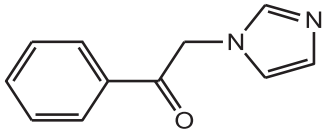
bis(benzimidazol-1-yl)methane (bzm)



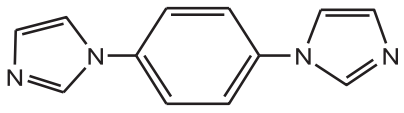
1-(2-(1H-benzimidazol-1-yl)ethyl)-1H-benzimidazole (bezm)



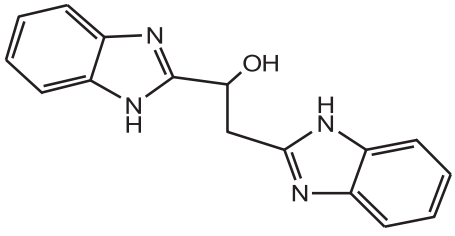
1-(3-(1H-benzimidazol-1-yl)propyl)-1H-benzimidazole (bpzm)



2-(imidazol-1-yl)-1-phenylethanone (impeta)



3,6-bis(imidazol-1-yl)pyridazine) (pdim)



1,2-bis-(1*H*-benzoimidazol-2-yl)-ethanol (bezel)

HCl HBr $HClO_4$ H_3PO_4

Scheme 1. H-bond tectons discussed in this paper.