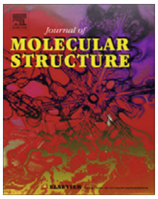
Journal of Molecular Structure 998 (2011) 192–197

Contents lists available at ScienceDirect

Journal of Molecular Structure

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



# Crystal structure of hydrates of imidazolium salts

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## ARTICLE INFO

*Article history:*
Received 4 April 2011
Received in revised form 19 May 2011
Accepted 19 May 2011
Available online 25 May 2011

*Keywords:*
X-ray diffraction
Crystal packing
H-bonding network
Imidazolium salts

## ABSTRACT

Single crystal X-ray structures of three imidazolium salts were examined. In contrast to imidazolium salt **1** possessing an ester group which created a network of C—H···halide–anion interactions with a linear array of imidazolium and the corresponding counter anions, unique network structures were observed in imidazolium salts **2** and **3** with long alkyl chains and with carboxy moieties, respectively. Water molecules were incorporated in their H-bonding networks. Water molecules were wedged into the two neighboring halide anions to create square units which acted as a bridge to connect the two adjacent C—H···halide–anion networks of imidazolium moieties and counter anions.

## 1. Introduction

Recently, much attention has been paid to the chemistry of imidazolium salts as ionic liquids [1–6] and ionic liquid crystals [7,8]. Imidazolium-based ionic liquids are the most commonly used ionic liquids for extraction and reaction solvents because of their nonflammability and nonvolatility. Imidazolium salts are also utilized as ionic liquid crystalline materials. Stable liquid crystals could be generated from imidazolium salts substituted with long alkyl chains due to an efficient microphase separation of ionic cores (imidazolium moieties) from flexible lipophilic alkyl chains. They are investigated as potential ion conductive materials [9–11] and lithium-ion batteries [12]. X-ray crystallographic studies of imidazolium salts have been studied in order to design novel functionalized ionic liquids [13–20]. We are interested in the arrangement of counter anions for elucidation of the assembled structures in ionic liquid crystals. However, the examples of their structural elucidation are limited [21–25]. In the course of our study on imidazolium-based ionic liquid crystals [26], we have found and examined the crystal structure of the hydrated imidazolium salts. In this paper, we report on the array of the imidazolium cations and the corresponding counter anions associated with water molecules.

In some cases, the way of packing in the crystal structures of imidazolium salts involves clipping of counter anions with the two adjacent cationic imidazolium rings. Counter anions are located near the surface of imidazolium rings via ionic interactions. The ionic layer thus created is separated by the layers of aliphatic substituents [21,22,27–29] (Fig. 1a). This microphase separation is applied to the generation of stable ionic liquid crystals. The other type of packing includes C—H···halide–anion interacted networks, the association of hydrogen atoms at the 2- and 4-positions of the imidazolium moiety with the counter anions. Imidazoliums and counter anions are aligned alternately in a horizontal way [17] (Fig. 1b).

The network structure we will discuss here involves the incorporation of water molecules. There are a few reports on single crystal X-ray structures of hydrated imidazolium halides [30–34]. Water molecules were incorporated in their H-bonding networks. We found a unique arrangement of water molecules. Water molecules were wedged into the two neighboring halide anions to create four-membered square units which acted as bridges to connect the two adjacent C—H···halide–anion interacted networks of imidazolium moieties and counter anions (Fig. 1c). A similar type of the hydrate of the imidazolium salt was reported on the imidazolium substituted with a long mono-alkyl chain [33]. An interesting water clusters were reported in the crystal structures of metal complexes of zwitterionic type imidazoliums [18,35]. Apart from imidazolium salts, halide anions associate with water to form halide–water clusters. Supramolecular assembly of chloride–water tapes and bromide–water chains were reported in the crystal structure of terpyridine salts [36]. An interesting dimeric capsule of an arene based tripodal amide receptor was formed using fluoride–water clusters as a template [37]. Chloride–water clusters were generated in MOFs (Metal Organic Frameworks) with free carboxylic acid sites [38].

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doi:10.1016/j.molstruc.2011.05.032

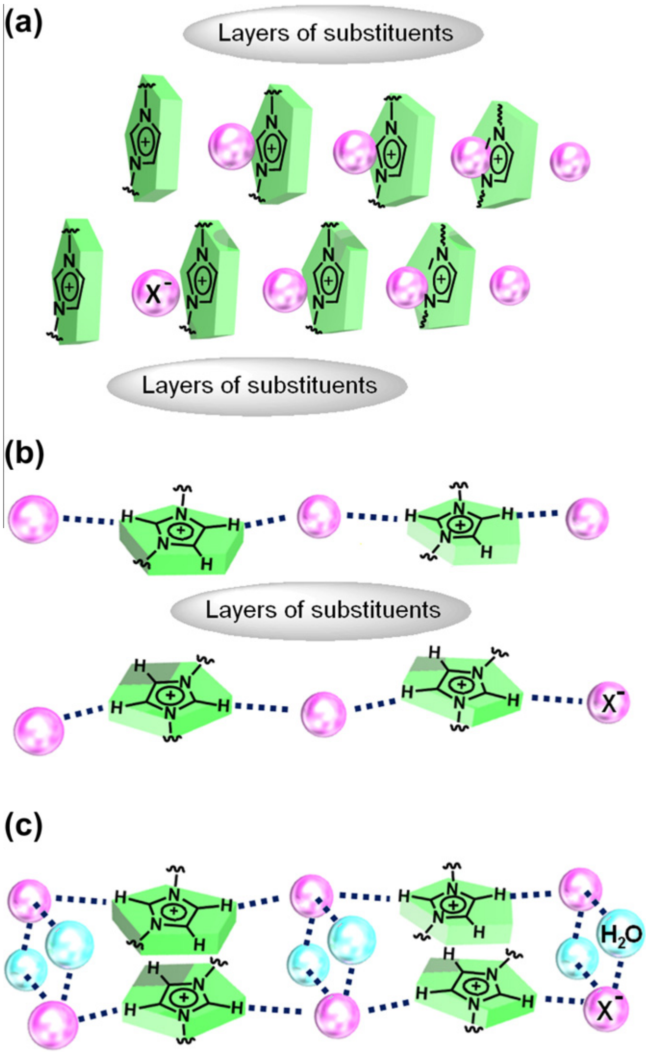

**Fig. 1.** Schematic representation of three types of network structures of imidazolium salts in their crystal structures. Counter anions and water molecules are indicated by pink and sky-blue spheres, respectively. (a) A sandwich structure in which counter anions are clipped by the neighboring imidazolium moieties, (b) networks of imidazolium-counter ion pairs in a horizontal way, and (c) networks with incorporation of water molecules via H-bonding. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

## 2. Experimental

### 2.1. General

All the reagents and solvents employed were commercially available and used as received without further purification. X-ray diffraction data for the crystals were measured on CCD diffractometers. Data collections were carried out at low temperature [150 K for **1** and **3**$\cdot(H_2O)_2$, and 100 K for **2**$\cdot H_2O$] by using liquid nitrogen. All structures were solved by direct methods SHELXS-97 [39] and the non-hydrogen atoms were refined anisotropically against $F^2$, with full-matrix least squares methods SHELXL-97 [39]. Hydrogen atoms were included as their calculated positions. The position of hydrogen atoms of a water molecule in the crystals of **2**$\cdot H_2O$ were determined based on the electronic density distribution. About a water molecule in the crystals of **3**, the position of hydrogen atoms were not calculated. Crystal data for **1** (CCDC 819420), **2**$\cdot H_2O$ (CCDC 819422), and **3**$\cdot(H_2O)_2$ (CCDC 819421) are presented in Table 1.

### 2.2. Synthesis

The imidazolium salts **1** and **3** were prepared by conventional methods described below. The known salt **2** was prepared according to the literature [40].

### 2.3. 3-(2-Ethoxy-2-oxoethyl)-1-(3,4,5-trimethoxybenzyl)-1H-imidazol-3-ium bromide (1)

A mixture of 1-(3,4,5-tris(methoxy)benzyl)imidazole (0.10 g, 0.40 mmol) and ethyl 2-bromoacetate (0.13 mL, 1.2 mmol) in acetonitrile (10 mL) was refluxed for 12 h at 90 °C. The solvent was removed under reduced pressure. The mixture was purified by column chromatography on silica gel (eluent: $CHCl_3$/MeOH = 9/1) to give **1** (0.14 g, 0.34 mmol) in 84% yield as a white powder. Single crystals were obtained by recrystallization from chloroform/acetonitrile. Mp. 142–144 °C: $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 1.32 (t, $J = 7.1$ Hz, 3H), 3.84 (s, 3H), 3.90 (s, 6H), 4.28 (q, $J = 7.1$ Hz, 2H), 5.42 (s, 2H), 5.43 (s, 2H), 6.76 (s, 2H), 7.30 (t, $J = 1.4$ Hz, 1H), 7.41 (t, $J = 1.4$, 1H), 10.57 (s, 1H): $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 14.42, 50.73, 54.15, 57.03, 61.21, 63.40, 106.76, 122.00, 124.07, 128.54, 138.26, 139.08, 154.27, 166.44: IR(KBr) $\nu$ 3172, 3110, 2985, 2841, 1739, 1560, 1510, 1430, 1235, 1163: HRMS (ESI) calcd for $C_{17}H_{23}O_5N_2$ $[M-Br]^+$ 335.1601, found 335.1595.

### 2.4. 1,1′-(1,4-phenylenebis(methylene))bis(3-(carboxymethyl)-1H-imidazol-3-ium) bromide (3)

A mixture of 1,1′-(1,4-phenylenebis(methylene))bis(3-(2-ethoxy-2-oxoethyl)-*1H*-imidazol-3-ium) bromide (0.200 g, 0.35 mmol) in 1 M aqueous HCl solution (30 mL) was refluxed for 30 min. The solvent was removed under reduced pressure and the remaining solid was washed with acetone and THF to give **3** (0.18 g, 0.34 mmol) as a white powder in 98% yield. Single crystals were obtained by recrystallization from water with diffusion of acetone vapor. Mp. > 270 °C (dec.): $^1H$ NMR (300 MHz, $D_2O$) $\delta$ 4.97 (s, 4H), 5.34 (s, 4H), 7.34 (s, 4H), 8.80 (s, 2H): $^{13}C$ NMR (75 MHz, $D_2O$) $\delta$ 50.53, 52.95, 122.67, 124.34, 129.78, 134.74, 137.36, 170.43: IR (KBr) $\nu$ 3160, 3140, 3120, 3026, 2767, 2681, 2575, 2485, 1733, 1567, 1396, 1199, 1170 $cm^{-1}$: MS (ESI) calcd for $C_{18}H_{19}O_4N_4$ $[M-2Br-H]^+$ 355.1401, found 355.1399.

## 3. Results and discussion

The structures of Imidazolium salts **1**–**3** examined are shown in Scheme 1. The salts **1** and **2** possess phenyl group substituted with trialkoxy groups. The latter is known to show liquid crystallinity

**Table 1**
Crystallographic data for imidazolium salts **1**–**3**.

| Salt | 1 | 2$\cdot H_2O$ | 3$\cdot(H_2O)_2$ |
|---|---|---|---|
| Formula | $C_{17}H_{23}BrN_2O_5$ | $C_{47}H_{87}ClN_2O_4$ | $C_{18}H_{24}Br_2N_4O_6$ |
| Crystal system | Triclinic | Triclinic | Triclinic |
| Space group | $P-1$ | $P-1$ | $P-1$ |
| $a$ (Å) | 8.8843(9) | 7.209(4) | 7.0222(8) |
| $b$ (Å) | 10.8379(11) | 8.242(5) | 8.6568(10) |
| $c$ (Å) | 11.1756(11) | 43.03(2) | 9.1506(11) |
| $\alpha$ (°) | 104.141(1) | 85.385(7) | 75.440(1) |
| $\beta$ (°) | 107.610(1) | 87.767(7) | 84.095(1) |
| $\gamma$ (°) | 103.817(1) | 68.883(6) | 87.955(1) |
| $V$ (Å$^3$) | 935.90(16) | 2377(2) | 535.51(11) |
| $D_c$ (Mg m$^{-3}$) | 1.474 | 1.089 | 1.712 |
| $Z$ | 2 | 2 | 1 |
| $T$ (K) | 150 | 100 | 150 |
| $R_1$ $[I > 2\sigma(I)]$ | 0.0300 | 0.0624 | 0.0508 |
| $wR_2$ $[I > 2\sigma(I)]$ | 0.0804 | 0.1639 | 0.1588 |