Synthesis and properties of acetamidinium salts

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Acetamidines are starting materials for the synthesis of many chemical substances such as imidazoles, pyrimidines, and triazines, which are further used as biochemically active compounds and as well as energetic materials. The aim of this study was to synthesize and characterize a range of acetamidinium salts in order to overcome the inconveniences associated with acetamidinium chloride, which is the only commercially available acetamidinium salt. The acetamidinium salts were synthesized and characterized using elemental analysis, mass spectrometry, NMR, and in the case of energetic salts DTA. The structures of previously unknown acetamidinium salts were determined by X-ray diffraction analysis. The hygroscopicities in 90% humidity of eight acetamidinium salts were evaluated at 90% humidity. The different hygroscopicity values were values of hygroscopicity are corroborated by the structures determined using X-ray analysis. A The acetamidinium salts with 2D layered structures (acetamidinium nitrate, formate, oxalate, and dinitromethanide) show a lack of hygroscopicity, and whereas compounds with 3D type of structures (acetamidinium chloride, acetate, sulfphate, and perchlorate) and possessing rather large cavities are quite hygroscopic.

Commented [A1]: **Tip:** Collocations are combinations of words often used together. When certain expressions do not sound "natural" or "right", consult a dictionary for usage.

For example,
Original: We *arrived on* the same conclusion.
Revised: We *arrived at* the same conclusion.

Introduction

Acetamidines are the starting materials for in the synthesis of many chemical substances such as imidazoles, pyrimidines, and triazines, which are further used as for biochemically active compounds [1-5]. Acetamidine In the field of energetic materials, acetamidine is the a starting material for the synthesis of 2-methoxy-2-methylimidazolidine-4,5-dione [6] and 2-methylpyrimidine-4,6-diol [7-9]. Both are further transformed into 2,2-dinitroethene-1,1-diamine (FOX-7, DADNE), which is an energetic material with low sensitivity to external stimuli [6,10]. The free base acetamidine is hygroscopic. It decomposes into ammonia and acetonitrile at higher temperatures [11], and produces acetamidinium carbonate for during one day at room temperature when stored in contact with air [12]. Therefore, it is unsuitable as a starting material for the synthesis, and the use of an acetamidinium salt is necessary.

Acetamidinium chloride is the The most commonly used and commercially available salt of acetamidine is acetamidinium chloride (1). It was is prepared using by the Pinner method with from acetonitrile and alcohol in the presence of hydrogen chloride, followed by addition of ammonia to the intermediate iminoether [13]. The reaction of acetonitrile with Co cobalt or Ni nickel nitrates and oximes produces gives acetamidinium nitrate (**2**) [14,15]. Acetamidinium acetate 3 is an An easily accessible acetamidine salt is acetamidinium acetate (**3**), prepared via by the reaction of triethyl orthoacetate, ammonia, and ammonium acetate [16]. This method is convenient, for both for laboratory and industrial use, and or the acetate may be further transformed into other salts, such as e.g. formate (**4**) [17], sulfphate (**5**) [18], or dinitromethanide (**6**) [19]. Several Many synthetic routes to for acetamidines have been reviewed [20,21].

However, the The main disadvantage of acetaminium chloride is its relatively high hygroscopicity. The release of the free base in methanol by the use of sodium methoxide will produces sodium chloride, which is partly soluble in this solvent (~1 g/100 ml).[22] The presence of any chloride source is unfavourable in certain syntheses such as, e.g. nitrations, and its complete removal is tedious.[6]
Herein, we describe the synthesis, X-ray structure, hygroscopicity, and thermal stability of some of the acetamidine salts listed in Figure 1.