



Synthesis and properties of novel acetamidinium salts

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Acetamidines are starting materials for the synthesis of many chemicals, some of which go on to be substances, such as imidazoles, pyrimidines and triazines, which are further used for synthesis of biochemically active compounds and as well as energetic materials. Acetamidinium chloride, which is hygroscopic, is currently one of the only commercially available acetamidinium salts. The aim of this study was to synthesize and characterize a range of acetamidinium salts that will in order to allow overcome the inconvenience connected associated with acetamidinium chloride to be avoided acetamidinium chloride, which is the only commercially available acetamidinium salt. Acetamidinium salts were synthesized. The acetamidinium salts were characterized and characterized by with elemental analysis, mass spectrometry, NMR and—in the case of energetic salts—differential thermal analysis (DTA). The structures of several previously unknown acetamidinium salts were determined established by X-ray diffraction (XRD) analysis. Hygroscopicities of eight of the acetamidinium salts were monitored over time at a 90% humidity of eight acetamidinium salts were evaluated. The different hygroscopicity values obtained of hygroscopicity were corroborated by the results of crystal structure analysis structures determined by X-ray analysis. We found that the acetamidinium salts with two-dimensional (2D) layered structures were (acetamidinium nitrate, formate, oxalate and dinitromethanide) show a lack of not highly hygroscopic. These were the nitrate, formate, oxalate, and dinitromethanide acetamidinium salts. However, the compounds with a 3D-type of structure containing rather large cavities were highly hygroscopic. These were the (acetamidinium chloride, acetate, sulphate, and perchlorate acetamidinium salts) and possessing rather large cavities are quite hygroscopic.

Introduction

Acetamidines are used as starting reagents starting materials in the synthesis of a number of many chemicals substances, such as imidazoles, pyrimidines, and triazines, which are further then used for synthesis of biochemically active or energetic compounds.^[1-3] In the field of energetic materials, acetamidine is employed in a starting material for the synthesis of 2-methoxy-2-methylimidazolidine-4,5-dione^[4] and 2-methylpyrimidine-4,6-diol.^[7-9] Both are further transformed to 2,2-dinitroethene-1,1-ethenediamine, also known as FOX-7 or DADNE, which is an energetic material explosive with low sensitivity to external stimuli.^[6,10]

The free-base form of acetamidine is hygroscopic and it decomposes into ammonia and acetonitrile at higher

temperatures,^[11] and produces a acetamidinium carbonate is formed within during 24 hours one day when acetamidine is exposed to air at room temperature^[12] when stored in contact with air.^[12] Therefore, it is therefore unsuitable as a starting material, so for synthesis and the use of an acetamidinium salt is necessary for synthetic reactions.

Acetamidinium chloride (1) is one of the only commercially available salts of acetamidine and is the most commonly used^[13] and commercially available salt of acetamidine is acetamidinium chloride (1). It is prepared by the Pinner method from acetonitrile and alcohol in the presence of hydrogen chloride, followed by addition of ammonia is added to the iminoether intermediate to yield 1.^[13] Many synthetic routes for acetamidines have been reviewed.^[20,21] Reaction of acetonitrile with cobalt or nickel nitrates and oximes gives yields acetamidinium nitrate (2).^[14,15] Another easily accessible acetamidine salt is acetamidinium acetate (3), is readily prepared by the reaction from of triethyl orthoacetate, ammonia, and ammonium acetate.^[16] This method is convenient for, both for laboratory and industrial scale synthesis, and use of the acetate may be further transformed into yield other salts, such as the formate (4),^[17] sulphate (5),^[18] and dinitromethanide salts (6).^[19] Many synthetic routes for acetamidines have been reviewed [20,21].

The main disadvantage of acetamidinium chloride is that it is its relatively hygroscopic high hygroscopicity. The

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formation/release of the free base in methanol by the use of sodium methoxide produces/will produce sodium chloride, which is partially soluble in the solvent (~1 g/100 mL).²² The presence of any chloride source is unfavourable in certain syntheses, such as e.g. nitrations, and its/the complete removal of chloride is tedious.⁶

Here we describe the synthesis, crystal/X-ray structure, hygroscopicity, and thermal stability of several of the acetamidinium salts shown in Fig. 1.

Fig. 1 Acetamidinium salts analyzed in this study.

Results and discussion

Synthesis

We previously reported a procedure for the preparation of acetamidinium sulphate (5) from 1 via an ion exchange reaction from acetamidinium chloride (1) was earlier described by us.²² For our purposes, it may be considered a universal method for the preparation of acetamidinium salts from 1 (Fig. 2). We used this procedure to synthesize was now used for the synthesis of the nitrate (2), as well as acetamidinium oxalate (7). Based on a previously reported method for the preparation of 5,¹⁸ we obtained acetamidinium perchlorate (8) from 3 and perchloric acid. Thus, it may be considered as a universal method for the preparation of acetamidinium salts starting from 1 (Figure 2).

The method used in the preparation of (5),¹⁸ starting from acetamidinium acetate and based on the reaction of the latter with an acid stronger than acetic acid, was now successfully used in the preparation of acetamidinium perchlorate (8) from 3 and perchloric acid. Acetamidinium perchlorate (8) was also prepared from 5 by an ion exchange reaction with barium perchlorate in water (Figure 3). Acetamidinium formate (4) was prepared from trimethyl orthoacetate and ammonium formate. A similar method has been published earlier by Taylor for preparation of 3.¹⁶

Fig. 2 Preparation of acetamidinium nitrate (2), sulfate (5), and oxalate (7) from 1.

Fig. 3 Preparation of 8 from 5 by ion exchange.

The method starting with acetamidinium acetate (3) based on the reaction with a stronger acid than the one we used (acetic acid) for acetamidinium sulphate (5)¹⁸ was now successfully used for preparation of acetamidinium perchlorate (8). This salt was also prepared from 5 by an ion exchange reaction with barium perchlorate in water (Figure 3).

Acetamidinium formate (4) was prepared from trimethyl orthoacetate and ammonium formate. A similar method has been published earlier by Taylor for preparation of 3.¹⁶

Hygroscopicities

The acetamidinium salts were weighed and stored under 90% humidity at 30 °C²³ for 1–21 days. Samples of ammonium acetate (10), guanidinium nitrate (11), and guanidinium chloride (12) were stored under identical conditions. The

Hygroscopicities of the samples of acetamidinium salts were determined at 90% humidity and 30 °C²³ and to be the percent weight increase compared with the weight of the original sample. The results are summarized in Table 1, and the changes in hygroscopicity (%) over time are plotted in the comparison of these results with ammonium acetate (10), guanidinium nitrate (11) and guanidinium chloride (12) are represented as the weight increase compared with the weight of the original sample, expressed in %. The results are given in Figure 4, and values for certain days are presented in Table 1. In the case of compounds with known structures determined by X-ray diffraction (XRD) techniques analysis, information about the spatial structure is also included. The influence of the structure on hygroscopicity is discussed later in this report.

Table 1 Hygroscopicities of acetamidinium and other salts.

Fig. 4 Changes in the hygroscopicities of acetamidinium salts over time.

X-Ray crystallography

The acetamidinium cations may frequently serve as a counterions for a wide variety of anions, like simple halogenides, carboxylates, and complex metal anions and others. The parent acetamidinium is characterized by reveals large cavities and an extensive network system of hydrogen bonding within its structure. The distances between the pivot carbon atom and the amino and imido nitrogen atoms are pivot carbon atom 1.344 Å and 1.298 Å, respectively and the amino and imido nitrogen atoms are rather distinct (1.344 Å for C-NH₂ and 1.298 Å for C = NH group).²⁴

The hydrogen bridging observed in acetamidinium chloride (1),²⁶ acetamidinium sulfate (5),¹⁸ and an one of the polymorphs of acetamidinium (2-hydroxyethoxy)acetate polymorph²⁵ results in three-dimensional (acetamidinium chloride (1),²⁶ and acetamidinium sulphate (5)¹⁸ revealed 3D) structures with large cavities. On the other hand, acetamidinium tetrazolate²⁷ and acetamidinium dinitromethanide (6)¹⁹ show are two-dimensional (2D), the staircase-like 2D structures. Interesting examples are acetamidinium hexafluorosilicates, germanates, stannates, and titanates²⁸ are interesting examples of 2D structures. Other examples include of the Re-Se cluster-acetamidinium adducts,²⁹ in which where multicentre NH...F or NH...Se contacts were found.

For two of the compounds studied in this study, we used XRD analysis to determine the molecular/crystal structures were determined by X-ray crystallography techniques of several acetamidinium salts. Acetamidinium oxalate (7), shown in Figure 5, has a 2D structure with comprised of interconnected layers interconnected with not too extensive/limited H-bonding. In contrast, Acetamidinium perchlorate (8, Figure 6) has a 3D structure with layers that were interconnected with by extensive H-bonding.

Fig. 5 Hydrogen bridging in the 2D structure of acetamidinium oxalate (7).

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Fig. 6 The 3D structure of acetamidinium perchlorate (8).

The perchlorate and oxalate structures were rather unique in the set of among the acetamidinium structures determined/examined. The molecular structure of the acetamidinium oxalate consists of is made up of two mutually similar acetamidinium units and one oxalate ion. All these ions participate in both compounds are interconnected by extensive H-hydrogen bonding systems. In the oxalate (7), eight- and fourteen-membered rings are formed by 7, as shown in (Figure 7). Acetamidinium perchlorate (8) primarily forms rings with 22 members, as shown in (Figure 8). The primarily forms rings with 22 members, as shown in (Figure 8). In our analysis, the acetamidinium C-NH₂ group formed an H-bond with a single oxygen atom in perchlorate, and the distance between the pivot carbon atom and the NH₂ moiety in this group was 1.323(3) Å. The other nitrogen-containing group formed two H-bonds with the perchlorate ion. The distance between the pivot carbon and nitrogen atoms in this group was the distances between the pivot carbon atom and the NH₂ moiety are rather different – 1.323(3) Å for the C-NH₂ group bonded by H bonds only to one oxygen atom of the perchlorate ion, and 1.297(4) Å for the C-NH₂ group bonded by two H bonds to the perchlorate ion. The molecular structure of the oxalate is made up of two mutually similar acetamidinium units and one oxalate ion. All these ions in both compounds are interconnected by extensive hydrogen bonding systems. In the oxalate (7), eight- and fourteen-membered rings are formed (Figure 7). The twenty two-membered rings are the main element of the perchlorate (8) structure (Figure 8).

In the oxalate structure, the distances between differences between the respective pivot carbon and nitrogen atoms were even greater at 1.339(5) Å and 1.280(5) Å. Our observations were not consistent, which disagree with delocalization, and they differed from values concept and the data found in the literature, which fall between (1.302 and 1.312 Å). In these groups/reports, the H-bonds to the oxalate moiety are equidistant.

Fig. 7 Ring structures formed by hydrogen bridges between ions in acetamidinium oxalate (7).

Fig. 8 Ring structures formed by hydrogen bridges between ions in acetamidinium perchlorate (8).

In light of the results of the XRD analysis, The molecular structure of the oxalate is made up of two mutually similar acetamidinium units and one oxalate ion. All these ions in both compounds are interconnected by extensive hydrogen bonding systems. In the oxalate (7), eight- and fourteen-membered rings are formed (Figure 7). The twenty two-membered rings are the main element of the perchlorate (8) structure (Figure 8).

From a study of the above mentioned data and motifs, in combination with the hygroscopicity data presented in Table 1, on the hygroscopicities of the compounds, it is clearly

indicate that the 2D layered structures compounds containing with layered 2D (counterions linked by H bridges) structures counterions linked by H-bridges – 2, 4, 6, 7, and 11 – were not hygroscopic. (2, 4, 6, 7, and 11; for 7, see Figure 9) are not hygroscopic. illustrates the [] of 7. On the other hand, the compounds that displayed 3D structures – (1, 3, 5, and 8) – were more hygroscopic. For 8, see Figure 10 shows the [] for 8.) have rather high hygroscopicities. This was probably due to caused by an easier incorporation of water molecules into the larger cavities of in the compounds with 3D structures, compared to the intercalation of water into the compounds with 2D structures.

Fig. 9 2D structure (7).

Fig. 10 3D structure (8).

NMR spectroscopy

The NMR data for acetamidinium salts 2, 4, 7, and 8 obtained with deuterated water (D₂O) are summarized in Table Table 2. A closer inspection of the proton NMR spectra measured in D₂O revealed that there is an equilibrium between deuterated and non-deuterated molecules, which were identified by marked (strongly decreased in the signal intensities of acidic protons intensity of the signals of the acidic protons). The equilibrium is shifted almost entirely to the side of the deuterated forms, indicating that sample (approximately 98%) of the molecules were deuterated. These observations contradicted findings is a contradiction between these observations and those published by Kopylovich,¹⁴ wherein which no deuteration was described, and two signals per 2H were observed.

Table 2 Results of NMR analysis of acetamidinium salts.

On the other hand, the positive direction of the equilibrium was reversed in mixtures containing deuterated dimethyl sulfoxide d₆ (DMSO-d₆), in which where approximately 90% of the compounds were in non-deuterated form can be found for in all of the samples measured/analyzed. With the exception of acetamidinium formate (4)

In all cases (excluding 4 in DMSO-d₆), two distinct/separated broadened signals/peaks belonging to the 2 × NH₂H arrangement were observed, which were probably due attributable to the delocalization of the positive charge throughout the amidinium group. The only exception is acetamidinium formate 4 in DMSO-d₆ where produced one a single broad signal/peak, which represented comprising all four NH protons bound to nitrogen was detected. The interactions within several acetamidinium complexes were studied by Tominey and Krechl using NMR, XRD analysis, and quantum chemical treatment.^{17,27} Our NMR results were This is in accordance with the observations published by Krechl¹⁷ and similar to the results obtained by Tominey²⁷ for acetamidinium tetrazolate complexes. These observations may have been due to This may be caused by differences in the interactions

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between ~~the~~ formate anion and amidinium groups in ~~de~~ifferent solvents. ~~The interactions inside some acetamidinium complexes were studied by Tominey and Krechl by means of NMR, X-ray analysis and quantum chemical treatment.~~^{17,27}

Differential thermal analysis

Acetamidinium nitrate (**2**), acetamidinium dinitromethanide (**6**), and acetamidinium perchlorate (**8**) are energetic materials. The ~~have~~ potential ~~for~~ use ~~is~~ in pyrotechnic applications, where they may replace guanidinium ~~nitrate or perchlorate salts (nitrate or perchlorate)~~. The ~~acetamidinium salts difference is the~~ have higher carbon contents ~~than of acetamidinium salts compared to the their analogous guanidinium analogs, as ones (replacement of the an~~ amino group in guanidines ~~is replaced~~ by a methyl group) ~~in acetamidine~~. Nevertheless, acetamidinium salts ~~still~~ have a relatively high nitrogen content. Compounds **6** and **8** ~~have exhibited~~ acceptable decomposition temperatures ~~as determined by measured by differential thermal analysis (DTA). The DTA thermograms from the compounds are shown in Fig. 11.~~ Both the nitrate (**2**) and the perchlorate (**8**) decomposed ~~upon~~ melting. ~~Thus,~~ ~~the~~ decomposition temperatures of **2** and **8** ~~were~~ considered as being 183 °C and 248 °C, respectively. ~~(Figure 11).~~ The maxima of ~~the~~ decomposition ~~ranges~~ ~~s~~ for **2** and **8** ~~were~~ 255 °C and 390 °C, respectively. ~~For~~ ~~in~~ comparison, ~~decomposition of~~ guanidinium nitrate ~~on the same thermal stability device~~ started ~~to decompose~~ at 270 °C, ~~and~~ guanidinium perchlorate ~~started to decompose~~ at 350 °C, ~~using the same thermal stability device.~~

Conclusions

Acetamidinium salts were synthesized and characterized by elemental analysis, electrospray mass spectrometry, ~~and~~ NMR. ~~The and, in the case of~~ energetic salts ~~were also examined, by~~ with DTA. The structures of ~~several~~ previously unknown acetamidines ~~have been~~ ~~were~~ identified ~~proved~~ by X-ray diffraction ~~by~~ XRD analysis. Hygroscopicities ~~of eight acetamidinium salts were determined at 90% humidity in 90% humidity of eight acetamidinium salts have been evaluated. The results of the different values of~~ hygroscopicity analysis ~~were~~ are corroborated by the structures ~~al~~ ~~determinations~~ ~~performed~~ by XRD-ray analysis. The acetamidinium salts with 2D layered structures ~~were~~ are not hygroscopic, while ~~the~~ acetamidinium salts with 3D layered structures ~~were highly~~ are quite hygroscopic.

Conflicts of interest

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Acknowledgements

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Notes and references

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