Synthesis and Characterization of Ammonium Acesulfamate

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Ammonium acesulfamate, $(NH_4)C_4H_4NO_4S$, was prepared by the reaction of acesulfamic acid and ammonium carbonate in aqueous solution, and characterized by elemental analysis and ^1H and ^{13}C NMR spectroscopy. Its crystal and molecular structure was determined by single-crystal X-ray diffraction methods. The substance crystallizes in the orthorhombic space group *Pnma* with $Z = 4$ molecules per unit cell. The NH_4^+ ion generates medium to strong hydrogen bonds with the carbonylic oxygen, the iminic nitrogen and the sulfonyl oxygen atoms of the acesulfamate anion. The FTIR spectrum of the compound was also recorded and is briefly discussed.

Key words: Ammonium Acesulfamate, Synthesis, Crystal Structure, FTIR Spectra

Introduction

Food additives are substances added intentionally to foodstuffs to perform certain functions such as to impart color, sweeten or preserve. They play an essential role in the modern food industry, supporting quality and safety [1]. In this context, artificial sweeteners are profusely used in food, beverage, confectionary and pharmaceutical products throughout the world [1].

Acesulfame-K, the potassium salt of 6-methyl-1,2,3-oxathiazin-4(3*H*)-one-2-2-dioxide, discovered by Karl Clauss [2, 3], is one of the most widely used non-caloric artificial sweeteners and has about 200 times the sweetening capacity of sucrose [3, 4]. Its general chemical and biological properties have been thoroughly investigated [1 – 3], and its crystal structure has also been determined [5].

From the chemical and structural points of view, the acesulfamate anion (Fig. 1) bears some resemblance to saccharin (1,2-benzothiazole-3(2*H*)-one-1,1-dioxide), whose coordination capacity has been intensively exploited during the last years (for a recent review *cf.* ref. [6]). The acesulfamate anion presents different potential coordination sites: the iminic nitrogen, the carbonylic oxygen and the two sulfonyl oxygen atoms,

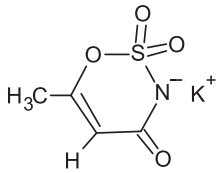

Fig. 1. Formula drawing of potassium acesulfamate.

and it can act as a monodentate, bidentate or bridging ligand, in the same way as saccharinate.

Recently, a series of metal complexes of acesulfamate have been reported [7 – 15], and in order to contribute to a better and wider knowledge of this interesting anion it seemed valuable to investigate also some of its most simple salts. In this context, we have now prepared and thoroughly characterized the respective ammonium salt.

Results and Discussion

Synthesis of ammonium acesulfamate

The compound was prepared by reaction of aqueous solutions of stoichiometric amounts of acesulfamic acid and ammonium carbonate, under the conditions described in the Experimental Section.

Crystal and molecular structure of the compound

An ORTEP [16] plot of the salt is shown in Fig. 2, and intramolecular bond lenghts and angles are given in Table 1. The observed distances and angles are comparable to those found in the potassium salt [5] and in choline acesulfamate [17]. Particularly, the short C3–C4 distance of 1.306(4) Å confirms the formal double bond character expected for this link. The carbonyl >C=O double bond distance is 1.237(3) Å and the sulfonyl d(S=O) distance is 1.418(2) Å. The other ring single bond lengths are d(C–O) = 1.393(4), d(O–S) = 1.634(3), d(S–N) = 1.537(2), d(C–N) = 1.332(3), and d(C–C) = 1.456(4) Å. All three above mentioned acesulfamate binding sites act as acceptors of medium to strong hydrogen bonds with neighboring NH_4^+ cations [$d(NH_4\cdots O_{sulf})$ = 2.048, $d(NH_4\cdots O_{carb})$ = 2.068 and $d(NH_4\cdots N)$ = 2.362 Å].

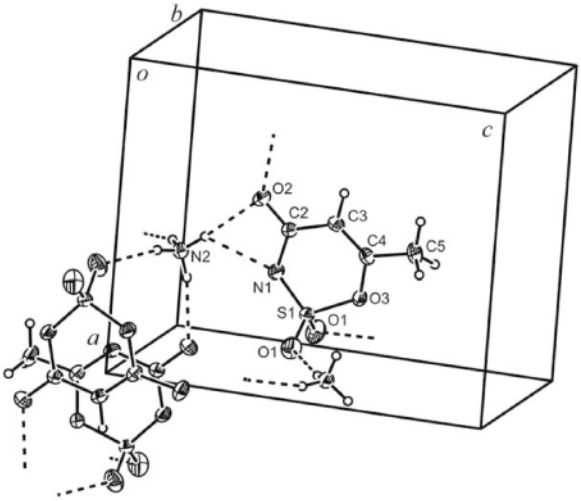

Fig. 2. View of the structure of the ammonium acesulfamate salt showing the labeling of the non-H atoms and their displacement ellipsoids at the 30% probability level. The hydrogen bonds are indicated by dashed lines.

Table 1. Bond lengths (Å) and angles (deg) of ammonium acesulfamate[a].

C(2)–O(2)	1.237(3)	N(1)–C(2)–C(3)	118.8(2)
C(2)–N(1)	1.332(3)	C(4)–C(3)–C(2)	124.9(2)
C(2)–C(3)	1.456(4)	C(3)–C(4)–O(3)	119.8(2)
C(3)–C(4)	1.306(4)	C(3)–C(4)–C(5)	128.6(3)
C(4)–O(3)	1.393(4)	O(3)–C(4)–C(5)	110.1(3)
C(4)–C(5)	1.485(4)	C(2)–N(1)–S(1)	124.1(2)
N(1)–S(1)	1.537(2)	C(4)–O(3)–S(1)	117.9(2)
O(1)–S(1)	1.418(2)	O(1′)–S(1)–O(1)	113.5(2)
O(3)–S(1)	1.634(3)	O(1′)–S(1)–N(1)	112.33(8)
S(1)–O(1′)	1.418(2)	O(1)–S(1)–N(1)	112.33(8)
		O(1′)–S(1)–O(3)	94.7(1)
O(2)–C(2)–N(1)	118.7(3)	O(1)–S(1)–O(3)	114.2(1)
O(2)–C(2)–C(3)	122.5(2)	N(1)–S(1)–O(3)	108.6(1)

[a] The primed oxygen atom is related to the unprimed one by the mirror-plane symmetry operation: x, $-y+1/2$, z.

Vibrational spectra

The FTIR absorption spectrum of the salt is shown in Fig. 3 and the proposed assignments are presented in Table 2. The assignments were performed on the basis of a recent experimental and DFT-theoretical study of potassium acesulfamate [18] and are briefly discussed as follows:

The general spectral pattern of the acesulfamate anion is totally comparable to that found for the potassium salt, and only very small differences in the position and/or intensity of some bands are observed. Vibrational modes related to ν(C=O) and ν(C−C) vibrations are strongly coupled and result in two of the most intense IR bands.

Bands related to the vibrational modes of the sulfonyl moiety appear at similar energies as in sodium saccharinate and in saccharinato complexes [6, 19].

The spectrum of ammonium acesulfamate has, obviously, an additional number of bands, in comparison to the potassium salt, generated by the NH_4^+ cation.

The detailed analysis of the bands related to this cation shows some remarkable aspects. The strong and broad band observed in the highest energy region can

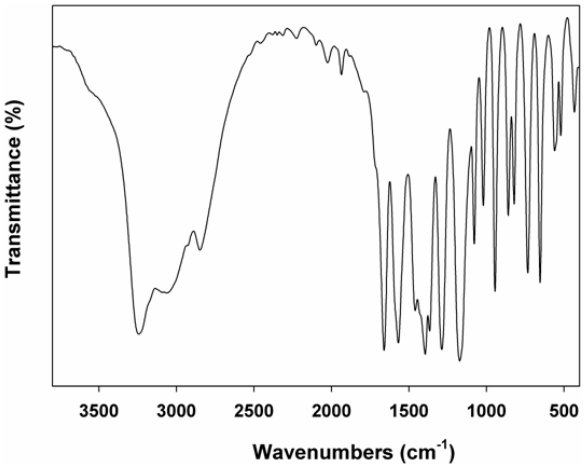

Fig. 3. FTIR spectrum of ammonium acesulfamate in the spectral range between 4000 and 400 cm^{-1}.

Table 2. Assignment of the FTIR spectrum of ammonium acesulfamate[a].

Band position (cm^{-1})	Proposed assignment
3242 vs, 3062 s, br	$\nu_3(NH_4^+)$
2849 w	$2\nu_4(NH_4^+)$
2100 vw, 2025 w, 1935 w	see text
1765 sh	$\nu_4+\nu_6(NH_4^+)$
1660 vs, 1590 sh/1569 vs	$\nu(C{=}O)+\nu(C{-}C)$ring
1459 m, 1431 w	$\delta(CH_3)+\nu_4(NH_4^+)$
1393 vs	$\delta(CH_3)$
1370 s	$\nu(NC)+\nu(OC)+\delta(CCH)$
1288 vs	$\nu_{as}(SO_2)$
1171 vs/1158 sh	$\nu_s(SO_2)+\nu(SN)$
1080 s	$\delta(CH_3)$
1021 s	$\nu(OC)+\nu(SN)$
946 vs	$\nu(OC)+\nu(C{-}CH_3)$
861 s	τ(ring)
821 s	$\nu(SN)+\nu(C{-}C)+\delta(NCO)$
734 vs	τ(ring)
655 vs	δ(ring)
563 m	$\delta(SO_2)+\delta$(ring)
547 m, 521 m, 434 m	δ(ring)

[a] vs, very strong; s, strong; m, medium; w, weak; vw, very weak; br, broad; sh, shoulder.

be assigned to the split anti-symmetric ν_3 stretching vibration of NH_4^+, although the symmetric mode, ν_1, is eventually also activated and overlapped by the ν_3 components. The antisymmetric deformational mode of the cation, ν_4, is overlapped by other relatively strong bands in the region around 1400 cm^{-1}. This band multiplet is somewhat more complex in the present case than for the corresponding potassium salt. Interestingly, no evidences are found for an activation of the symmetric deformation, ν_2, although a weak shoulder seen at *ca.* 1690 cm^{-1}, on the high energy side of the strong 1660 cm^{-1} band, may be eventually related to this mode.

The activation of some combination and overtone modes is usually regarded as a proof that the NH_4^+ cation does not rotate freely in the crystal structure [20, 21], as is the case in the compound investigated here. One of the expected overtones is clearly seen as a weak band at 2849 cm^{-1}, which can be assigned to $2\nu_4$. The very weak feature observed at 1765 cm^{-1} may be related to one of the expected combinations involving ν_4 and an external (lattice) mode located at about 360 cm^{-1} ($\nu_4+\nu_6$ in Waddington's nomenclature [20]). The other usually observed combination mode ($\nu_2+\nu_4$) is expected at around 3070 cm^{-1} and is surely overlapped by the strong ν_3 components.

The weak and very weak bands found at 2100, 2025 and 1935 cm^{-1} could not be assigned with certainty. Thus, they probably originate also from combination or overtone modes.

Experimental Section

Materials and measurements

Potassium acesulfamate was supplied by Fluka and ammonium carbonate, along with the other employed reagents were from Merck, analytical grade, and were used as purchased. Elemental analysis of the compound was performed with a Carlo Erba model EA 1108 elemental analyzer. The infrared absorption spectra were recorded on a FTIR Bruker EQUINOX-55 spectrophotometer in the spectral range between 4000 and 400 cm^{-1}, using the KBr pellet technique. NMR spectra were recorded in D_2O using a Bruker Avance 300 instrument. Chemical shifts are reported in ppm downfield from tetramethylsilane. ^{1}H NMR spectra were recorded at 300 MHz and ^{13}C NMR spectra at 75 MHz.

Synthesis of the compound

Acesulfamic acid was prepared as described by Velaga *et al.* [22], as follows: To 5.00 g of potassium acesulfamate dissolved in a small portion of water (*ca.* 15 mL), 6 mL of concentrated HCl was added drop-wise. The generated acid was extracted with 20 mL of ethyl acetate. After evaporation of the solvent in air a colorless solid was deposited. It was recrystallized twice from ethyl acetate, generating a deposit of needle-like colorless crystals, after slow evaporation of the solvent in air (m. p. 122 – 124 °C).

For the synthesis of the ammonium salt, 0.33 g (2.0 mmol) of acesulfamic acid was dissolved in 15 mL of distilled water and heated to 75 °C. To this solution, 0.10 g (1.0 mmol) of $(NH_4)_2CO_3$ was slowly added, under constant stirring. After this addition, the solution was stirred for another 30 min at the same temperature, and finally it was left to evaporate in air. After a few days a colorless powder, highly soluble in water, was collected and recrystallized from water (yield: *ca.* 0.25 g). The purity of the salt was confirmed by elemental analysis and NMR spectroscopy. – Analysis: $C_4H_8N_2O_4S$ (180.18): calcd. C 26.64, H 4.44, N 15.55; found C 26.58, H 4.50, N 15.50. – ^{1}H NMR: δ (ppm) = 2.02 (s, 3H, CH_3), 5.58 (s, 1H, =C–H). – ^{13}C NMR: δ (ppm) = 18.96 (CH_3), 100.98 (=C–H), 164.18 (>C=O), 172.22 (=C–Me). These data are practically identical to that measured for the potassium salt and also to those reported for choline acesulfamate [17]. Single crystals adequate for X-ray diffraction studies were selected from the crystalline mass employing a microscope.

Table 3. Crystal data and structure refinement results for ammonium acesulfamate.

Empirical formula	$C_4H_8N_2O_4S$
Formula weight	180.18
Crystal dimension, mm^3	$0.39 \times 0.28 \times 0.19$
Temperature, K	297(2)
Crystal system	orthorhombic
Space group	*Pnma*
a, Å	9.5047(6)
b, Å	6.9273(6)
c, Å	11.5255(6)
Volume, Å^3; *Z*	758.86(9); 4
Calculated density, g cm^{-3}	1.58
Absorption coefficient, mm^{-1}	0.4
F(000), e	376
θ-range for data collection, deg	3.43 – 26.99
Index ranges	$-1 \leq h \leq 12$, $-5 \leq k \leq 8$, $-14 \leq l \leq 14$
Reflections collected	2041
Independent reflections / R_{int}	884 / 0.0223
Observed reflect. [$I > 2\,\sigma(I)$]	757
Max. / min. transmission	0.9288 / 0.8610
Refinement method	Full-matrix least-squares on F^2
Data/ restraints/ parameters	884 / 0 / 88
Goodness-of-fit on F^2	1.085
Final indices *R*1 / *wR*2 [$I > 2\,\sigma(I)$]	0.0406 / 0.1027
Final indices *R*1 / *wR*2 (all data)	0.0473 / 0.1101
Largest peak / hole, e Å^{-3}	0.34 / –0.30

Crystal structure determination

The X-ray diffraction measurements were performed on an Oxford Xcalibur, Eos, Gemini CCD diffractometer with graphite-monochromatized MoK_α ($\lambda = 0.71073$ Å) radiation. X-Ray diffraction intensities were collected (ω-scans with ϑ- and κ-offsets), integrated and scaled with the CrysAlis Pro [23] suite of programs. The unit cell parameters were obtained by least-squares refinement (based on the angular settings for all collected reflections with intensities larger than seven times the standard deviation of measurement errors) using CrysAlis Pro. Data were corrected for extinction and empirically for absorption employing the multi-scan method implemented in CrysAlis Pro. The structure was solved by Direct Methods with Shelxs-97 [24] and the molecular model refined by the full-matrix least-squares procedure on F^2 with Shelxl-97 [25]. The atoms are related by a crystallographic mirror plane. However anisotropic refinement of the acesulfamate anion showed that its molecular model is better described as a positionally disordered structure where the ring oxygen atom departs slightly from the plane (0.321 Å) giving rise to two split mirror-related positions. All hydrogen atoms were located in a difference Fourier map phased on the heavier atoms and refined at their found positions with isotropic displacement parameters. Crystal data and structure refinement results are summarized in Table 3.

CCDC 976866 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac-uk/data_request/cif.

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