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Structural and IR-spectroscopic characterization of magnesium acesulfamate

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Abstract: Magnesium acesulfamate, $\text{Mg}(\text{C}_4\text{H}_4\text{NO}_4\text{S})_2 \cdot 6\text{H}_2\text{O}$, was prepared by the reaction of acesulfamic acid and magnesium carbonate in aqueous solution, and characterized by elemental analysis. Its crystal structure was determined by single crystal X-ray diffraction methods. The substance crystallizes in the triclinic space group $P\bar{1}$ with one molecule per unit cell. The FTIR spectrum of the compound was also recorded and is briefly discussed. Some comparisons with other simple acesulfamate and saccharinate salts are also made.

Keywords: crystal structure; FTIR spectra; magnesium acesulfamate; synthesis.

1 Introduction

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

From the chemical and structural points of view, the acesulfamate anion 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. [5]). Similar to saccharinate, the acesulfamate anion presents different

potential coordination sites (the imine nitrogen, the carbonyl oxygen and the two sulfonyl oxygen atoms), and it can act as a mono-dentate, bi-dentate or bridging ligand. This versatility has been widely exploited and numerous metal complexes containing the acesulfamate ligand have been reported and characterized during the last 10 years (cf., for example, [6] and references therein).

Notwithstanding, simple salts of this anion have only been investigated most recently. We could characterize ammonium acesulfamate [7] and have found that the isotopic sodium, rubidium and cesium acesulfamates [8], as well as the corresponding thallium(I) salt [9], are isostructural to one another and to the previously known potassium salt [4]. Also, calcium [10], strontium and barium [11] acesulfamates have recently been prepared and characterized.

In order to advance in the knowledge of the alkaline-earth acesulfamates, we have now prepared and investigated the crystal structure and vibrational-spectroscopic behavior of the corresponding magnesium salt.

2 Results and discussion

Mg acesulfamate has been obtained by the reaction of MgCO_3 with an aqueous solution of acesulfamic acid, using a general procedure recently developed by us for the synthesis of simple acesulfamate salts [7–9], as described in the Experimental Section. The obtained $[\text{Mg}(\text{H}_2\text{O})_6]$ ($\text{C}_4\text{H}_4\text{NO}_4\text{S}$)₂ crystallizes in the triclinic space group $P\bar{1}$ with one molecule per unit cell.

An ORTEP [12] drawing of the salt is shown in Fig. 1, and the bond distances and angles in the acesulfamate anion are listed in Table 1. These are in accordance with values reported for the alkaline metal salts [4, 8], the heavier alkaline-earth salts [10, 11] and the thallium(I) salt [9]. Particularly, the short C3–C4 distance of 1.322(4) Å confirms the formal double bond character expected for this link. The carbonyl $>\text{C}=\text{O}$ double bond distance is 1.255(3) Å, and sulfoxide S=O distances are 1.420(2) and 1.429(2) Å. The ring single bond lengths are $d(\text{C}-\text{O}) = 1.401(3)$ Å, $d(\text{O}-\text{S}) = 1.605(2)$ Å, $d(\text{S}-\text{N}) = 1.563(2)$ Å, $d(\text{C}-\text{N}) = 1.354(3)$ Å and $d(\text{C}-\text{C}) = 1.450(4)$ Å.

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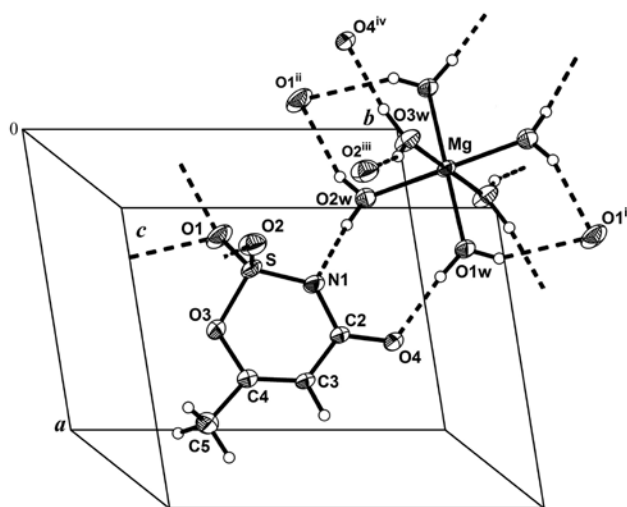


Fig. 1: View of hexaquamagnesium acesulfamate salt showing the labeling of the non-H atoms and their displacement ellipsoids at the 30 % probability level. Hydrogen bonds are indicated by dashed lines. Symmetry operations: (i) $x, y + 1, z$; (ii) $-x, -y + 1, -z + 1$; (iii) $-x, -y + 1, -z + 2$; (iv) $x - 1, y, z$.

Table 1: Intra-molecular bond lengths (Å) and angles (deg) of the acesulfamate anion in $[\text{Mg}(\text{H}_2\text{O})_6](\text{acesulfamate})_2$.

C(2)–O(4)	1.255(3)	N(1)–C(2)–C(3)	120.0(2)
C(2)–N(1)	1.354(3)	C(4)–C(3)–C(2)	123.3(3)
C(2)–C(3)	1.450(4)	C(3)–C(4)–O(3)	120.7(3)
C(3)–C(4)	1.322(4)	C(3)–C(4)–C(5)	128.4(3)
C(4)–O(3)	1.401(3)	O(3)–C(4)–C(5)	110.9(2)
C(4)–C(5)	1.482(4)	C(2)–N(1)–S	119.5(2)
N(1)–S	1.563(2)	C(4)–O(3)–S	117.1(2)
O(1)–S	1.429(2)	O(2)–S–O(1)	116.1(2)
O(2)–S	1.420(2)	O(2)–S–N(1)	112.8(2)
O(3)–S	1.605(2)	O(1)–S–N(1)	110.4(1)
		O(2)–S–O(3)	106.3(1)
O(4)–C(2)–N(1)	118.8(2)	O(1)–S–O(3)	103.6(1)
O(4)–C(2)–C(3)	121.2(2)	N(1)–S–O(3)	106.8(1)

These bond lengths can be compared with those of the free acesulfamic acid. This crystallizes in two polymorphic forms, one triclinic space group $P\bar{1}$ with $Z = 2$ molecules per unit cell, and the other one monoclinic space group

$P2_1/c$ with two (symmetry-independent) molecules per asymmetric unit ($Z = 8$) [13]. Referred to the better refined triclinic form, the major change in bonding in the structure of the acesulfamate ion in the magnesium salt occurs at the S–N bond, which upon loss of the proton shortens by 0.066 Å (about 30 times the standard error σ). A much smaller shortening is observed in the N–C and S–O bond lengths ($-0.028 \text{ Å} = -9\sigma$ and $-0.012 \text{ Å} = -6\sigma$, respectively).

The Mg(II) ion is situated at a crystallographic inversion center in an octahedral environment of water molecules which are coordinated through their oxygen lone pairs [Mg–O_w bond distances of 2.050(2), 2.072(2) and 2.085(2) Å, and O_w–Mg–O_w angles of 91.0(1)°, 91.4(1)° and 89.4(1)°]. This prevents the Mg(II) ion from direct electrostatic interaction with the acesulfamate anion, as it happens in the calcium, strontium and barium salts [10, 11]. The ionic $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}/\text{Ace}^-$ interaction is mediated by hydrogen bonding involving as donors all three independent water molecules and as acceptors the nitrogen [$d(\text{OwH}\cdots\text{N}) = 1.943 \text{ Å}$, angle(Ow–H \cdots N) = 173.1°], carbonyl oxygen [OwH \cdots O(carb) distances of 2.690 and 2.698 Å, and Ow–H \cdots O(carb) angles of 171.5° and 169.6°] and sulfoxide oxygen [OwH \cdots O(sulf) distances from 2.839 to 3.040 Å and Ow–H \cdots O(sulf) angles from 148.7° to 162.1°] atoms of five neighboring acesulfamate anions (see again Fig. 1). The hydrogen bonding data are further detailed in Table 2.

Interestingly, in the related saccharinato complex, $\text{Mg}(\text{sac})_2 \cdot 7\text{H}_2\text{O}$ (triclinic space group $P\bar{1}$, $Z = 2$), the Mg(II) ion is octahedrally coordinated by five oxygen atoms from H₂O molecules and one oxygen atom from the CO group of one of the saccharinato anions [14]. There are seven independent types of water molecules, involved in hydrogen bonding with neighboring H₂O molecules and/or with the electron donor atoms from the saccharinato anions (N, O_{CO}, O_{SO2}). The O_w \cdots O and O_w \cdots N distances range from 2.714 to 3.046 Å and from 2.898 to 2.939 Å, respectively. Some of these distances are very close or practically identical to each other [14, 15].

The FTIR spectrum of $[\text{Mg}(\text{H}_2\text{O})_6](\text{Ace})_2$ is shown in Fig. 2. It is similar to those measured in the case of some

Table 2: Hydrogen bonds (distances in Å, angles in deg) in $[\text{Mg}(\text{H}_2\text{O})_6](\text{acesulfamate})_2$.

D–H	$d(\text{D}–\text{H})$	$d(\text{H}\cdots\text{A})$	$\angle(\text{D}–\text{H}\cdots\text{A})$	$d(\text{D}\cdots\text{A})$	A	Symmetry operation
O1W–H1A	0.86	1.84	171.5	2.690(3)	O4	
O1W–H1B	0.81	2.32	148.7	3.040(3)	O1	$x, y + 1, z$
O2W–H2A	0.88	1.94	173.1	2.817(3)	N1	
O2W–H2B	0.81	2.07	158.7	2.839(3)	O1	$-x, -y + 1, -z + 1$
O3W–H3A	0.79	2.13	162.1	2.894(3)	O2	$-x, -y + 1, -z + 2$
O3W–H3B	0.90	1.81	169.6	2.698(3)	O4	$x - 1, y, z$

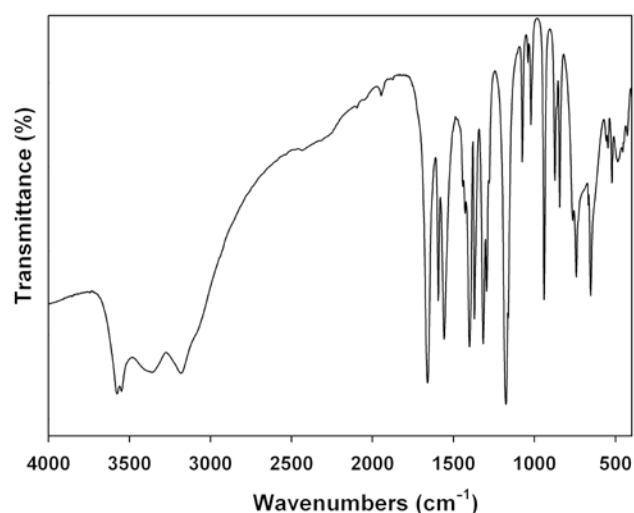


Fig. 2: FTIR spectrum of $[\text{Mg}(\text{H}_2\text{O})_6](\text{acesulfamate})_2$ in the spectral range between 4000 and 400 cm^{-1} .

of the previously investigated acesulfamate salts [8, 9]. The spectral assignment, presented in Table 3, was performed on the basis of a recent experimental and density functional theory study of potassium acesulfamate [16], additionally supported by our previous studies [7–9], and is briefly discussed in the following.

- The O–H stretching vibrations of the water molecules generate a strong and well-defined doublet and two additional strong and relatively broad bands, each accompanied by a weak shoulder. The presence of

Table 3: Assignment of the FTIR spectrum of $[\text{Mg}(\text{H}_2\text{O})_6](\text{acesulfamate})_2$,^a

Band position (cm^{-1})	Proposed assignment
3576 s/3549 s, 3403 sh/3363 s,br	$\nu(\text{OH}) (\text{H}_2\text{O})$
3181 s/3078 sh	$\nu(\text{OH}) (\text{H}_2\text{O})$
1660 vs, 1594 m/1558 vs	$\nu(\text{C}=\text{O}) + \nu(\text{C}-\text{C})$ ring
1442 vw, 1429 vw, 1401 vs	$\delta(\text{CH}_3)$
1370 vs	$\nu_{\text{as}}(\text{SO}_2)$
1317 vs, 1295 s	$\nu(\text{CN}) + \nu(\text{OC}) + \delta(\text{CCH})$
1176 vs, 1162 sh	$\nu_{\text{s}}(\text{SO}_2) + \nu(\text{SN})$
1075 m	$\delta(\text{CH}_3)$
1041 w/1022 m	$\nu(\text{OC}) + \nu(\text{SN})$
940 vs	$\nu(\text{OC}) + \nu(\text{C}-\text{CH}_3)$
874 m	$\tau(\text{ring})$
844 s	$\nu(\text{SN}) + \nu(\text{C}-\text{C}) + \delta(\text{NCO})$
764 w/742 m	$\tau(\text{ring})$
667 sh/653 s	$\delta(\text{ring})$
557 vw/547 w	$\delta(\text{ring}) + \delta(\text{SO}_2)$
521 m, 486 w	$\tau(\text{ring})$
455 m,br	$\rho_{\text{w}}(\text{H}_2\text{O})$
427 vw	$\tau(\text{ring})$

^avs, Very strong; s, strong; m, medium; w, weak; vw, very weak; br, broad, sh, shoulder.

these three doublets is compatible with the presence of the three structurally independent water molecules. The corresponding deformational modes, $\delta(\text{H}_2\text{O})$, are probably overlapping with bands found in the 1550–1660 cm^{-1} region. From the spectroscopic point of view the hydrogen bonds generated by these water molecules can be classified as H bonds of medium strength [17, 18].

- IR bands related to the CH and CH_3 stretching modes, expected in the 2800–3200 cm^{-1} range [19], are usually very weak, and could not be detected in the present case.
- As in the previously investigated cases, vibration modes related to $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{C})$ stretches are strongly coupled and result in two of the most intense IR bands. Interestingly, the second of these bands appears clearly split (the 1594/1558 cm^{-1} doublet), a fact which so far was only observed in the case of thallium(I) acesulfamate [9].
- The 1317/1295 cm^{-1} doublet is dominated by the $\nu(\text{CN})$ stretching vibration [16], coupled with some other motions. Also this band was found un-split in the previously investigated salts [7–9].
- Bands related to the vibrational modes of the sulfonyl moiety appear at somewhat higher energies than in sodium saccharinate and in saccharinato complexes [5, 15, 20, 21]. The corresponding $\nu_{\text{s}}(\text{SO}_2)$ vibration is partially coupled with other vibrational modes [16], as also found in the case of saccharinato complexes [20, 21].
- The medium-intensity band found at 455 cm^{-1} was assigned to the $\rho_{\text{w}}(\text{H}_2\text{O})$ wagging mode, in analogy with a similar band (460 cm^{-1}) assigned to this vibration in the case of $[\text{Mg}(\text{H}_2\text{O})_6]\text{SO}_4 \cdot \text{H}_2\text{O}$ [22].

3 Experimental section

3.1 Materials and measurements

Potassium acesulfamate was supplied by Fluka (Sigma-Aldrich, Steinheim, Germany), and magnesium carbonate and all the other employed reagents were from Merck (Darmstadt, Germany), of analytical grade, and were used as purchased. Elemental analyses were performed with a Carlo Erba (Milano, Italy) model EA 1108 elemental analyzer. The infrared absorption spectra were recorded on an FTIR-Thermo Nicolet 6700 spectrophotometer (Thermo Fisher Scientific, Waltham, MA, USA), equipped with a deuterated triglycine sulfate (DTGS) detector, in the spectral range between 4000 and 400 cm^{-1} , using the KBr pellet technique.

3.2 Synthesis of the compound

Acesulfamic acid was prepared as described by Velaga et al. [13], by treating an aqueous solution of potassium acesulfamate with concentrated HCl, followed by extraction of the generated acid with ethyl acetate and recrystallization of the solid acid twice from the same solvent (cf. also [7–9]).

For the synthesis of the Mg(II) salt, 2.0 mmol of acesulfamic acid was dissolved in 15 mL of distilled water and heated to 75 °C. To this solution, 1.0 mmol of MgCO₃ 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. 40 %). The purity of the salt was confirmed by elemental analysis: C₈H₂₀MgN₂O₁₄S₂ (456.69): calcd. C 21.02, H 4.38, N 6.13, S 14.04; found C 20.96, H 4.45, N 6.10, S 13.93. Single crystals adequate for X-ray diffraction studies were selected from the crystalline mass employing a microscope.

3.3 X-ray structure determination

X-ray measurements were performed on an Oxford Xcalibur, Eos, Gemini CCD diffractometer with graphite-monochromatized MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$). X-ray diffraction intensities were collected (ω scans with ϑ and κ offsets), integrated and scaled with the CRYSLISPRO [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 CRYSLISPRO. Data were corrected for extinction and empirically for absorption employing the multi-scan method implemented in CRYSLISPRO. The structure was solved with the intrinsic phasing procedure implemented in the SHELXT program [24]. The initial molecular model was refined with anisotropic displacement parameters employing the SHELXL program of the SHELX package [25].

The hydrogen atoms were found in a difference Fourier map phased on the heavier atoms. All but the methyl H atoms were refined at their found positions with isotropic displacement parameters. The CH₃ group was refined with the riding model, and the locations of the hydrogen atoms were optimized by treating them as a rigid body which was allowed to rotate around the corresponding C–CH₃ bond maximizing the sum of the residual electron density at their calculated positions. As a result, the methyl group converged to a staggered angular conformation. Crystal

Table 4: Crystal data, X-ray diffraction data and refinement results for [Mg(H₂O)₆](acesulfamate)₂.

Empirical formula	C ₈ H ₂₀ MgN ₂ O ₁₄ S ₂
Formula weight	456.69
<i>T</i> , K	297(2)
Crystal dimensions, mm ³	0.423 × 0.390 × 0.181
Crystal shape and color	Colorless fragment
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> , Å	6.9479(7)
<i>b</i> , Å	8.5986(9)
<i>c</i> , Å	8.740(1)
α , deg	68.48(1)
β , deg	78.394(9)
γ , deg	81.264(9)
Volume, Å ³	474.07(9)
<i>Z</i>	1
Calculated density, g cm ⁻³	1.60
Absorption coefficient, mm ⁻¹	0.4
<i>F</i> (000), e	238
θ range data collection, deg	3.61–26.99
Index ranges <i>hkl</i>	–8 ≤ <i>h</i> ≤ 6 –10 ≤ <i>k</i> ≤ 10 –10 ≤ <i>l</i> ≤ 11
Reflections collected	3791
Independent reflections/ <i>R</i> _{int}	2025/0.0453
Observed reflections [<i>I</i> > 2σ(<i>I</i>)]	1511
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	2015/0/153
<i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0527/0.1293
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.0711/0.1536
Goodness of fit on <i>F</i> ²	1.071
Largest peak/hole, e Å ⁻³	0.52/–0.58

data, data collection procedure and structure refinement results are summarized in Table 4.

CCDC 1413111 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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