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The crystal structure, vibrational spectra and DSC measurements of mono-β-alaninium nitrate

Ivan Němec*, Róbert Gyepes, Zdeněk Mička

Department of Inorganic Chemistry, Charles University, Albertov 2030, 128 40 Prague 2, Czech Republic

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Abstract

An X-ray structural analysis of mono- β -alaninium nitrate has been carried out. The substance crystallizes in an orthorhombic system in the space group $Pca2_1$, a = 14.8135(11) Å, b = 7.3338(5) Å, c = 11.9121(12) Å, V = 1294.12(18) Å³, Z = 8, R = 0.0361 for 1299 observed reflections. The asymmetric unit contains two β -alaninium cations (NH₃⁺ CH₂CH₂COOH) and two nitrate anions (NO₃⁻). The whole crystal structure is formed by β -alaninium dimers (linked by two intermediate asymmetrical hydrogen bonds of length 2.64 Å) and nitrate anions connected by a system of hydrogen bonds, in which all the hydrogen atoms of the NH₃⁺ groups participate. Fourier transform infrared (FTIR) and FT Raman spectra of natural and deuterated crystals were recorded and interpreted. The FTIR spectra were studied down to a temperature of 90 K. Differential scanning calorimetry (DSC) measurements were carried out in the temperature range 95–370 K. No phase transition was found in this temperature range by DSC and FTIR. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Crystal structure; Vibrational spectra; Phase transition

1. Introduction

The family of ferroelectric compounds of the triglycine sulfate (TGS) [1] type, i.e., generally addition compounds of amino acids with inorganic oxyacids, have been intensely studied and technically utilized materials for a number of years. TGS and its deuterated analogue, together with diglycine nitrate (DGN) [2], are the best known representatives of this interesting group of substances. All ferroelectric materials of this type are characterized by the presence of short O–H···O hydrogen bonds (shorter than 2.45 Å) connecting the carboxyls of glycine, which participate

* Corresponding author. Tel.: + 42-2-2195-111; Fax: + 42-2-291958; e-mail: agnemec@prfdec.natur.cuni.cz

in a complex phase transition mechanism between the paraelectric and ferroelectric modifications.

In the representatives of this group that are known so far, addition compounds of glycine predominate over the other amino acids. For example, for the simplest n-amino acid β -alanine, the crystal structure of only one compound has been published, β -alanine phosphate (*P*2₁/*n*, *a* = 16.115(20) Å, *b* = 5.829(2) Å, c = 8.019(5) Å, $\beta = 93.60(6)^\circ$, Z = 4, R = 0.038) [3].

The work reported here, which is part of our project searching for potential new ferroelectric substances based on the addition compounds of amino acids with inorganic oxyacids, is devoted to the study of mono- β -alaninium nitrate (M β AN) — the only addition compound found in the β -alanine-nitric acid-water system. In addition to solving the crystal structure, the vibrational spectra of M β AN and of

Table 1 Basic crystallographic data, data collection and refinement parameter

meters	
Empirical formula	$C_{2}H_{0}N_{2}O_{2}$
a	14 8135(11) Å
h	7.3338(5) Å
c	11.9121(12) Å
V	$1294.12(18) Å^3$
Z	8
D (calc.)	1.561 Mg m^{-3}
Crystal system	orthorhombic
Space group	$Pca2_1$
Mr.	152.12
μ (Mo K_{α})	0.149 mm^{-1}
F(000)	640
Crystal dimensions	$0.5 \text{ mm} \times 0.5 \text{ mm} \times 0.5 \text{ mm}$
Diffractometer and	Enraf-Nonius CAD4-MACH
radiation used	III, Mo K_{α} , $\lambda = 0.71073$ Å
Scan technique	$\omega - 2\theta$
No. and θ range of	$25, 13 \rightarrow 15$
reflections for lattice	
parameter	
refinement	
Range of h , k and l	$-18 \rightarrow 18, 0 \rightarrow 9, 0 \rightarrow 15$
No. of standard	3
reflections	
Standard reflections	60 min.
monitored in interval	
Intensity variation	2%
Total number of	2883
reflections measured	
θ range	2.75-26.95°
No. of independent	1478 (0.0122)
reflections (R_{int})	
No. of observed	1299
reflections	
Criterion for	$I > 2\sigma(I)$
observed reflections	
Absorption	none
correction	_ 2 2 2 2
Function minimized	$\sum w(F_0^2 - F_c^2)^2$
Weighting scheme	$w = \left[\sigma^2 (F_0^2) + (0.0544P)^2 + 0.45P\right]^{-1}$
	$P = (F_0^2 + 2F_c^2)/3$
Parameters refined	246
Value of R	0.0361
Value of <i>wR</i>	0.0974
Value of S	1.027
Extinction	0.0143(19)
coefficient	
Max. and min.	$0.295, -0.199 \ e \ \text{\AA}^{-3}$
heights in final $\Delta \rho$	
map	
Source of atomic	SHELXL97 [12]
scattering factors	
Programs used	SHELXL97 [12], PARST [13],
	pluto [14]

Table 2

Fractional atomic coordinates (\times 10⁴) and equivalent (for nonhydrogen atoms, $\times 10^3$) or isotropic (for hydrogen atoms, $\times 10^3$) displacement factors with standard deviations in brackets $U_{\rm eq} =$ $1/3\sum_{i}\sum_{j}U_{ij}a_{i}^{*}a_{j}^{*}\mathbf{a}_{i}\mathbf{a}_{j}$

	x	у	z	$U_{\rm eq}({\rm \AA}^2)$
O(1)	2718(2)	- 6276(3)	10981(3)	61(1)
O(2)	2978(2)	- 3411(3)	10831(3)	68(1)
O(3)	4031(2)	- 5242(5)	11428(4)	80(1)
O(4)	9679(2)	1284(4)	6278(4)	82(1)
O(5)	9665(3)	- 1524(4)	6385(4)	95(1)
O(6)	8493(2)	- 118(5)	5803(5)	85(1)
O(11)	3778(2)	- 4891(4)	8274(3)	56(1)
O(12)	4781(1)	- 3056(3)	9054(3)	45(1)
O(21)	8750(2)	114(3)	9069(4)	53(1)
O(22)	7777(1)	1921(3)	8164(2)	46(1)
N(1)	5970(2)	- 5196(4)	10565(3)	42(1)
N(2)	6551(2)	- 271(5)	6692(3)	39(1)
N(3)	3266(2)	- 4949(3)	11085(3)	40(1)
N(4)	9264(2)	- 138(4)	6138(3)	42(1)
C(11)	4547(2)	- 4561(4)	8736(3)	36(1)
C(12)	5141(2)	- 6210(4)	8864(3)	43(1)
C(13)	6053(2)	- 5770(4)	9377(3)	40(1)
C(21)	7990(2)	427(4)	8520(3)	36(1)
C(22)	7409(3)	- 1205(4)	8388(3)	43(1)
C(23)	6498(2)	- 788(4)	7888(3)	41(1)
H(11)	3360(4)	- 3670(8)	8210(5)	110(2)
H(21)	8990(3)	880(6)	9010(4)	61(14)
H(121)	5210(2)	- 6700(5)	8150(4)	52(11)
H(122)	4820(2)	- 7090(5)	9370(3)	37(9)
H(131)	6410(2)	- 6820(5)	9390(3)	40(8)
H(132)	6420(3)	- 4790(5)	8940(4)	52(13)
H(221)	7770(3)	- 1950(7)	8060(5)	72(14)
H(222)	7360(4)	- 1690(6)	9080(5)	82(14)
H(231)	6070(3)	- 11740(6)	7940(4)	58(11)
H(232)	6250(2)	- 9840(4)	8280(3)	27(9)
H(1N1)	5720(2)	- 6190(5)	10940(3)	43(10)
H(2N1)	6560(5)	- 4870(9)	11070(7)	130(3)
H(3N1)	5570(3)	- 4280(6)	10640(4)	53(11)
H(1N2)	6010(2)	- 120(4)	6450(3)	27(9)
H(2N2)	6810(3)	- 1120(7)	6240(5)	86(17)
H(3N2)	6840(3)	700(6)	6600(5)	74(14)

its deuterated and ¹⁵N-substituted analogues have been measured and interpreted. Fourier transform infrared (FTIR) measurements at low temperatures and differential scanning calorimetry (DSC) measurements over a broad temperature interval were carried out to elucidate the existence of possible phase transitions.

Table 3					
Bond lengths	(Å) :	and	selected	angles	(°)

Bond	Value	Angle	Value	Angle	Value
N(3)-O(1)	1.273(4)	O(2)-N(3)-O(1)	116.8(3)	C(11)-C(12)-H(122)	108(2)
N(3)–O(2)	1.243(4)	O(3)-N(3)-O(1)	119.2(3)	C(13)-C(12)-H(122)	109(2)
N(3)–O(3)	1.224(5)	O(3)-N(3)-O(2)	124.0(3)	H(131)-C(13)-H(132)	106(3)
N(4)-O(4)	1.221(4)	O(5)-N(4)-O(4)	115.9(4)	N(1)-C(13)-H(131)	106(2)
N(4)-O(5)	1.213(4)	O(6)-N(4)-O(4)	120.6(3)	C(12)-C(13)-H(131)	110(2)
N(4)-O(6)	1.210(5)	O(6)-N(4)-O(5)	123.5(4)	N(1)-C(13)-H(132)	109(3)
O(11)-C(11)	1.288(5)	O(12)-C(11)-O(11)	123.7(3)	C(12)-C(13)-H(132)	114(3)
O(12)-C(11)	1.217(4)	O(11)-C(11)-C(12)	114.2(3)	C(13)-N(1)-H(1N1)	105(2)
C(11)–C(12)	1.504(4)	O(12)-C(11)-C(12)	122.0(3)	C(13)-N(1)-H(2N1)	121(4)
C(12)-C(13)	1.517(4)	C(11)-C(12)-C(13)	113.0(3)	C(13)-N(1)-H(3N1)	111(3)
C(13)–N(1)	1.482(5)	N(1)-C(13)-C(12)	111.8(3)	H(1N1)-N(1)-H(2N1)	103(4)
C(12)-H(121)	0.93(4)	C(11)-O(11)-H(11)	112(3)	(1N1)-N(1)-H(3N1)	106(3)
C(12)-H(122)	1.00(4)	C(11)-C(12)-H(121)	106(2)	H(2N1)-N(1)-H(3N1)	108(4)
C(13)-H(131)	0.94(3)	C(13)-C(12)-H(121)	111(2)	C(23)-C(22)-H(222)	112(3)
C(13)-H(132)	1.04(4)	H(121)-C(12)-H(122)	110(3)	H(231)-C(23)-H(232)	105(3)
O(21)-C(21)	1.322(5)	O(22)-C(21)-O(21)	123.4(3)	C(22)-C(23)-H(231)	115(2)
O(22)-C(21)	1.217(4)	O(22)-C(21)-C(22)	122.6(3)	N(2)-C(23)-H(231)	107(4)
C(21)-C(22)	1.483(4)	O(21)-C(21)-C(22)	114.0(3)	C(22)-C(23)-H(232)	108(2)
C(22)-C(23)	1.507(5)	C(21)-C(22)-C(23)	113.5(3)	N(2)-C(23)-H(232)	109(3)
N(2)-C(23)	1.476(5)	C(22)-C(23)-N(2)	112.8(3)	H(1N2)-N(2)-H(2N2)	107(4)
C(22)-H(221)	0.85(5)	C(21)-O(21)-H(21)	105(4)	H(1N2)-N(2)-H(3N2)	109(4)
C(22)-H(222)	0.89(6)	H(221)-C(22)-(222)	102(5)	H(2N2)-N(2)-H(3N2)	106(5)
C(23)-H(231)	0.95(4)	C(21)-C(22)-H(221)	102(3)	C(23)-N(2)-H(1N2)	108(3)
C(23)-H(232)	0.91(4)	C(23)-C(22)-H(221)	120(4)	C(23)-N(2)-H(2N2)	115(3)
		C(21)-C(22)-H(222)	106(3)	C(23)-N(2)-H(3N2)	112(4)

Hydrogen bonds^a

Donor-H		Donor…acceptor	H…acceptor	Donor-H…acceptor
O(11)-H(11)	1.09(6)	$O(11)\cdots O(22)^i$	2.638(3) H(11)····O(22) ⁱ	1.55(6) O(11)-H(11)···O(22) ⁱ 178(4)
N(1)-H(1N1)	0.93(4)	$N(1)\cdots O(4)^{ii}$	2.882(4) $H(1N1)\cdots O(4)^{ii}$	1.99(4) N(1)-H(1N1)····O(4) ⁱⁱ 161(3)
N(1)-H(2N1)	1.09(7)	$N(1)\cdots O(1)^{iii}$	2.849(4) H(2N1)····O(1) ⁱⁱⁱ	1.91(7) N(1)-H(2N1)····O(1) ⁱⁱⁱ 142(5)
N(1)-H(2N1)	1.09(7)	$N(1)\cdots O(2)^{iii}$	3.161(5) H(2N1)····O(2) ⁱⁱⁱ	2.46(7) N(1)-H(2N1)····O(2) ⁱⁱⁱ 121(4)
N(1)-H(3N1)	0.91(4)	$N(1)\cdots O(5)^{iv}$	3.015(5) H(3N1)····O(5) ^{iv}	2.23(4) N(1)-H(3N1)····O(5) ^{iv} 144(3)
N(1)-H(3N1)	0.91(4)	N(1)…O(12)	2.967(4) H(3N1)O(12)	2.39(4) N(1)-H(3N1)····O(12) 122(3)
O(21)-H(21)	0.67(4)	$O(21)\cdots O(12)^{v}$	2.643(3) H(21)····O(12) ^v	1.98(5) $O(21)-H(21)\cdots O(12)^{v}$ 172(4)
N(2)-H(1N2)	0.86(3)	$N(2)\cdots O(4)^{i}$	2.913(4) $H(1N2)\cdots O(4)^{i}$	2.15(3) N(2)-H(1N2)····O(4) ⁱ 147(2)
N(2)-H(1N2)	0.86(3)	$N(2)\cdots O(5)^{i}$	$3.109(5) H(1N2) \cdots O(5)^{i}$	2.32(3) N(2)-H(1N2)···O(5) ⁱ 151(2)
N(2)-H(2N2)	0.91(6)	$N(2)\cdots O(1)^{vi}$	2.882(4) H(2N2)····O(1) ^{vi}	2.06(5) N(2)-H(2N2)····O(1) ^{vi} 150(4)
N(2)-H(3N2)	0.84(5)	$N(2)\cdots O(2)^{vii}$	2.972(4) H(3N2)····O(2) ^{vii}	2.21(5) N(2)-H(3N2)···O(2) ^{vii} 152(4)
N(2)-H(3N2)	0.84(5)	N(2)…O(22)	2.993(4) H(3N2)O(22)	2.49(6) N(2)-H(3N2)····O(22) 119(4)

^a Equivalent positions: (i) x - 1/2, -y, z; (ii) -x + 3/2, y - 1, z + 1/2; (iii) x + 1/2, -y - 1, z; (iv) -x + 3/2, y, z + 1/2; (v) x + 1/2, -y, z; (vi) -x + 1, -y - 1, z - 1/2; (vii) -x + 1, -y, z - 1/2.

2. Experimental

Crystals of M β AN were prepared by slow spontaneous evaporation of a solution of β -alanine (p.a., Loba Feinchemie) in nitric acid (Lachema, $1 \text{ mol } 1^{-1}$) (in a molar ratio of 1:1) at laboratory temperature. The colourless crystals obtained were collected under vacuum on an S4 frit, washed with ethanol and dried in air. The ¹⁵N-substituted (HNO₃) analogue was similarly prepared from a solution



Fig. 1. Asymmetric unit of M β AN. Dashed lines indicate hydrogen bonds.

containing $H^{15}NO_3$ (98% ¹⁵N, Aldrich) by crystallization in a dessicator over KOH. The deuterated compound ($ND_3^+CH_2CH_2COOD NO_3^-$) was prepared by repeated recrystallization of natural M β AN from D_2O (99%) in a dessicator over KOH.

The contents of carbon, nitrogen and hydrogen were determined with a Perkin–Elmer 240 C elemental analyser.

The infrared spectra of nujol and fluorolube mulls were recorded on an ATI Mattson Genesis FTIR spectrometer (2 cm^{-1} resolution, Beer–Norton medium apodization) in the 400–4000 cm⁻¹ region. Low-temperature measurements were carried out by the



Fig. 2. Packing scheme of M β AN. Dashed lines indicate hydrogen bonds.

nujol mull method in a low-temperature cell with KBr windows over the interval 298–90 K. The temperature was controlled by an Fe-Const. thermocouple. The analogue signal was processed on a PC using an AX5232 temperature measurement board.

The Raman spectra of polycrystalline samples were recorded on a Bruker RFS 100 FT Raman spectrometer (2 cm^{-1} resolution, Blackman–Harris fourterm apodization, 1064 nm NdYAG laser excitation,

Table 4 Analysis of the planarity of carboxyl groups in MβAN

y 1		0 1 1		
Equations of the p	lanes			
Carboxyl A	-5.92x - 1	.32y + 10.71z	= 7.27	
Carboxyl B $- 6.74x + 1.53y + 10.31z = 3.47$				
Atomic deviations	(Å)			
Carboxyl A		Carboxyl I	3	
C(12)	0.001	C(22)	0.001	
C(11)	-0.003	C(21)	-0.004	

0.001

0.001

0.02

O(21)

O(22)

 $H(21)^{a}$

0.001

0.002

-0.10

^a Atom not used to define plane.

O(11)

O(12)

H(11)^a



Fig. 3. β-Alaninium dimers in the MβAN crystal structure. Dashed lines indicate hydrogen bonds.

150 mW power at the sample) in the $50-4000 \text{ cm}^{-1}$ region.

The DSC measurements were carried out on a Perkin–Elmer DSC 7 power-compensated apparatus in the temperature region 95-370 K (helium or nitrogen atmosphere). A heating rate of 10 K min⁻¹ was selected to investigate approximately 10 mg of finely ground sample placed in an aluminium capsule.

X-ray data collection for the M β AN single crystal was carried out on an Enraf-Nonium CAD4-MACH III four-circle diffractometer (Mo K_{α} , graphite monochromator). The phase problem was solved by direct methods and the non-hydrogen atoms were refined anisotropically, by means of the full-matrix leastsquares procedure. The hydrogen atom positions were found from the difference Fourier map and their displacement factors were refined isotropically. The basic crystallographic data and details of the measurement and refinement are summarized in Table 1. A list of the observed and calculated structural factors and the anisotropic displacement factors are available from the authors upon request.

Table 5 Analysis of the planarity of nitrate anions in MβAN

Equations of the plan	es
Nitrate A	-4.61x + 1.01y + 11.20z = 10.42
Nitrate B	-5.02x + 0.45y + 11.18z = 2.22

Atomic deviations (Å)

Nitrate A		Nitrate B		
N(3)	- 0.002	N(4)	- 0.010	
O(1)	0.001	O(4)	0.003	
O(2)	0.001	O(5)	0.003	
O(3)	0.001	O(6)	0.004	

3. Results and discussion

3.1. The crystal structure of $M\beta AN$

The atomic coordinates are given in Table 2, and the bond lengths and angles, including those for the hydrogen bonds, are listed in Table 3. The atom numbering can be seen in Fig. 1 and the packing scheme is depicted in Fig. 2.

The asymmetric unit of M β AN contains two β alaninium cations (NH₃⁺CH₂CH₂COOH) and two nitrate anions (NO₃⁻). The crystal structure consists of β -alaninium dimers (linked by two intermediate asymmetrical hydrogen bonds of length 2.64 Å see Fig. 3) and nitrate anions connected by a system of hydrogen bonds, in which all the hydrogen atoms of the NH₃⁺ groups participate (see Table 3).

Both molecules of β -alaninium in the asymmetric unit exhibit corresponding increases in the length of the C–O(H) bonds (1.288 and 1.322 Å) compared with the C–O bonds (1.217 Å). Very similar bond length values for the protonated carboxyl groups (1.312 and 1.205 Å) have been published for the compounds of β -alanine phosphate [3]. The O–C–O bonding angle values (123.7 and 123.4°) are practically identical to the corresponding angles in

Table 6								
The results	of the	nuclear	site	group	analysis	for	МВА	N

C_{2v}^5		A_1	A_2	B_1	B_2
External modes	Acoustical	1		1	1
	Translational	11	12	11	11
	Librational	12	12	12	12
Internal nodes		84	84	84	84
	Total	108	108	108	108
Activity	IR	z		x	у
	Raman	$\alpha_x, \alpha_{yy}, \sigma_{zz}$	α_{xy}	α_{xz}	α_{yz}



Fig. 4. FTIR (nujol mull) and FT Raman spectra of natural MBAN.

 β -alanine phosphate (123.3°). In the non-protonated carboxyl group of pure β -alanine [4], this angle attains somewhat larger values (124.5°). Both carboxyl groups in the crystal structure of M β AN, including the hydrogen atoms, are planar and the maximum deviation from the carboxyl plane is that of atom H21, equal to 0.10 Å (see Table 4).

The bonding angles in the NH_3^+ group have values of 103° to 121°. The reason for the deviation from the expected values for tetrahedral angles (especially for the C–N–H bonds) apparently lies in the non-equivalent participation of all the hydrogen atoms of these groups in the hydrogen bond system of the N–H…O type (see Table 3). In addition to linear (two-centre)

Table 7

Correlation analysis of NO3 internal modes of MBAN crystal

Free ion modes	Deg. of freedom	Free ion symmetry D _{2b}	Site symmetry C1	Factor group symmetry	Vibration modes		Activity
			01	C _{2v}		IR	Raman
\mathbf{v}_1	8			A 1	$2v_1, 2v_2, 4v_3, 4v_4$	z	$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$
\mathbf{v}_2	8	A2''	Sit	A ₂	$2v_1, 2v_2, 4v_3, 4v_4$		α_{xy}
v ₃	8	E' /		B ₁	$2v_1, 2v_2, 4v_3, 4v_4$	x	α_{xz}
V4	8	E' /		B ₂	$2v_1, 2v_2, 4v_3, 4v_4$	у	α_{yz}

Table 8

FTIR and FT Raman spectra of M β AN (vs — very strong; s — strong; m — medium; w — weak; b — broad; sh — shoulder; ν — stretching; δ — deformation or in—plane bending; τ — torsional; γ — out—of—plane bending; ρ — rocking; ω — wagging; twi — twisting; subscript s — symmetric; subscript as — antisymmetric)

Assignment	IR		Raman	Raman Assignment	IR		Raman
	298 K	90 K			298 K	90 K	
$\nu N-H\cdots O$	3252 m	3263 s		$\delta_{as} NH_3^+$	1588 sh	1583 w	
		3222 m	3230 wb			1569 w	
		3198 m		$\delta_s \mathrm{NH}_3^+$	1510 m	1510 m	1500 w
		3163 w				1492 sh	
		3109 w		δCH_2	1462 m	1463 m	1468 w
		3075 w				1443 m	
$\nu_{as}CH_2$	3034 mb	3031 m	3020 w		1437 m	1434 m	
$\nu_{s}CH_{2}$			2991 m	vC-O	1414 s	1417 s	1418 m
$\nu_{as}CH_2$	2964 m	n.o. ^a	2967 s	νNO_3^-	1400 s	1403 s	1401 w
$\nu_s CH_2$			2940 s	$\delta CH_2, \omega CH_2$	1394 s	1397 s	
ν N–H···O, ν O–H···O	2904 m	n.o. ^a	2913 w			1361 s	
			2820 wb	ωCH_2	1349 s	1351 s	1354 w
	2769 m	2771 m	2777 w				1344 w
	2744 m	2743 m		$\nu_3 NO_3^-$, ωCH_2	1321 s	1326 s	1323 w
	2693 m	2699 m				1316 s	
	2637 m			twiCH ₂	1254 m	1257 m	1260 m
		2642 m		δC–O–H	1231 s	1234 s	1232 w
	2560 m	2573 m				1221 sh	
		2555 m	2560 wb	ρNH_3^+	1127 m	1127 m	1130 w
?	2444 w	2451 w		$\nu C^{\alpha} - C^{\beta}$	1093 m	1095 s	1096 w
	2367 w	2369 w		$\nu_1 NO_3^-$	1052 m	1054 m	1055 vs
		2323 w		$\rho NH_3^+, O-H\cdots O$	952 m	954 m	954 w
		2275 w		$\gamma O-H\cdots O$		937 m	
		2171 w		$ ho NH_3^+$	916 w	917 w	919 w
		2046 w		$\nu C - C^{\alpha}$	867 w	871 w	869 m
		1993 w				866 w	
		1946 w		$\nu_2 NO_3^-$	822 m	822 m	
		1906 w		үС–О–Н	813 m	814 m	814 m
$\nu_1 + \nu_4 \mathrm{NO}_3^-$		1798 w		$\nu_4 \mathrm{NO}_3^-$		732 w	
?	1774 w	1780 w			725 w	728 w	727 m
	1761 w	1764 w			711 w	712 w	714 w
	1730 w	1734 w	1731 w	δCOO	651 w	652 m	655 w
vC=O	1698 m	1702 m	1711 m	ωCOO	568 w	569 w	571 w
1		1691 m		$ au \mathrm{NH}_3^+$	507 w	509 w	510 w
$\delta_{as}NH_3^+$		1630 w	1648 w	δССО			383 w
	1610 m	1617 s	1611 w	lattice modes			129 s
		1605 w	1593 w				92 s

^a Not observed owing to nujol bands.

hydrogen bonds, four bifurcated (three-centre) hydrogen bonds of two types were found. The first type connects the N1 (N2) atom across hydrogen atom H2N1 (H1N2) with two oxygen atoms $O1^{iii}$ and $O2^{iii}$ (O4ⁱ and O5ⁱ) of the nitrates. The second type connects the N1 (N2) atom via hydrogen H3N1 (H3N2) with carboxyl oxygen O12 (O22) and nitrate oxygen O5^{iv} (O2^{vii}).

The bonding angles in the nitrate anions lie in the interval $115.9-124.0^{\circ}$ and the bond lengths have values from 1.210 to 1.273 Å. As expected, the longest N–O bond in the NO₃⁻ group is that to the O1 atom,



Fig. 5. FTIR (nujol mull) and FT Raman spectra of deuterated M β AN in the 400–1850 cm⁻¹ region.

which is one of four oxygen atoms that are simultaneously connected in two hydrogen bonds of the O···H-N type (see Table 3). In contrast, the shortest nitrate bond was found for one of the oxygens (O6) that does not participate in any of the hydrogen bonds. The second shortest bond (1.213 Å), N4–O5, clearly does not lie within this simple scheme of the dependence of the length of N-O bonds on the degree of participation in the system of hydrogen interactions, if we take into consideration that the O5 atom is connected in a pair of hydrogen bonds. A partial explanation for this situation could be the fact that these are two weak hydrogen bonds with a length of slightly over 3 Å (see Table 3). Both nitrate groups are almost ideally planar (see Table 5), and the maximum deviation from the planes is equal to 0.01 Å (atom N4).

3.2. Analysis of the vibrational spectra

The number of normal modes of the M β AN crystal

was determined by nuclear site group analysis [5]. Standard correlation methods [6] were used for a more detailed study of the expected vibrational features of the nitrate group. The results obtained are presented in Tables 6 and 7.

Orthorhombic M β AN crystals belong to the $Pca2_1$ (C_{2v}^5) space group with 36 atoms per asymmetric unit. All of the atoms occupy fourfold positions $\mathbf{a}(C_1)$. Four types of species present in the unit cell, two NO₃⁻ and two CH₃CHNH₃⁺COOH groups, occupying fourfold positions $\mathbf{a}(C_1)$, were considered in more detailed calculations of the internal and external modes.

On the basis of nuclear site group analysis (see Table 6), it can be expected that the vibrational spectra of the M β AN crystals will contain maximally fourfold (Raman spectra) to threefold (IR spectra) splitting of all the vibrational bands of each of the four species of the unit cell. However, with only a few exceptions, this level of splitting has not been observed even in low-temperature IR spectra and, in

Table 9 FTIR and FT Raman spectra of deuterated M β AN (for abbreviations, see Table 8)

Assignment	IR		Raman	Assignment	IR		Raman
	298 K	90 K			298 K	90 K	
?	3561 w	3561 w		?			1408 m
$2 \times \nu C = 0$	3370 w	3361 w		$\nu_3 NO_3^-$	1392 s	1392 s	1391 w
?		3251 m		ωCH ₂	1345 sb	1345 sb	1350 wb
	3235 m	3235 m	3238w	$\nu_3 NO_3^-$	1320 sb	1313 s	
	3060 mb	3052 m		twiCH ₂		1295 sh	1301 m
$\nu_{ac}CH_2$	3017 m	3017 m	3018 s		1254 s	1254 s	1256 w
v _a CH ₂			2990 s		1235 sh	1238 s	1237 m
v. CH ₂	2963 m	n o ^a	2965 vs		1227 s	1229 s	
v CH ₂	2934 m	n o ^a	2937 vs		1227 5	1215 m	
?	2931111	11.01	2798 w	δND_2^+	1171 s	1175 s	1172 w
	2760 w		2750 w	01123	1160 s	1162 s	11/2 w
	2687 w	2603 m	2704 W		1150 sh	1102 s	11/6 w
	2007 w 2633 w	2093 m	2655 w	uC^{α} C^{β} aCH	1006 m	1007 m	1005 w
	2035 W	2052 m	2055 W	$\nu c = c$, $\rho c n_2$	1090 III 1067 o	1077 m	1095 w
-NDO	2300 w	2308 III	2420	$\sim NO^{-}$	1057 s	1070 8	1052 va
$\nu N = D \cdots 0,$ $\nu O = D \cdots O$	2432.8	2438 8	2429 W	$\nu_1 NO_3$	1032 8	1054 8	1052 VS
	2413 m	2417 m		$\rho CH_2, \nu C-C$	1037 w	1039 m	
	2396 s	2399 s			1032 w	1034 w	
		2387 s	2385 m		1021 w	1023 m	1024 w
	2347 m	2353 m		δND_3^+ , ρCH_2 , $\nu C - N$	1005 s	1006 s	1008 w
	2320 m	2323 m	2318 w		925 wb	937 w	935 w
	2280 m	2273 m	2265 w	νC-C, δCOO	905 w	907 w	905 w
	2228 s	2223 s	2230 m	$\rho ND_3^+, \rho CH_2, \nu C-C$	863 w	864 w	861 w
	2175 sh	2180 s			854 m	857 m	853 w
		2162.8					846 w
	2110 m	2114 s	2116 w	$\nu_2 NO_2^-$	823 m	823 m	821 m
	2110 III	2103 s	2110	$_{0}ND_{2}^{+}$	813 sh	814 w	021 111
	2089 m	2092 s		prob3	015 51	808 w	
	2005 m	2052 s		$\gamma ODO \rho ND^+$	796 w	797 m	795 m
	1967 sh	1969 w		$_{\rm ND^+}$	770 w	773 w	773 w
	1907 SH	1909 w		μUD_3	750 w	763 w	760 w
	1000 w	1877 w		NO^{-}	739 W	705 w 745 m	700 w
		10// W		$V_4 NO_3$	744 w 728 m	743 III 721 m	745 w
	1924	1805 W			720 III 718 m	731 III 710 m	720 III 719 ab
	1824 W	1627 W			718 III	719 III 712 ···	/18 80
$\nu_1 + \nu_2$		1798 W			/12 m	/12 m	
$\nu_4 NO_3$		1705		2000		660	
?		1785 w		8000	663 m	668 s	662 w
	1775 w	1779 w			645 w	645 w	646 w
	1762 w	1764 w			622 m	622 s	625 w
		1727 sh		ωCOO	522 w	555 w	565 w
vC=O	1686 s	1686 s	1699 m				549 w
	1644 w	1645 m	1646 w	ρCOO	495 sh	498 w	
?	1564 w	1561 w			489 w	490 w	490 w
	1497 sh	1498 w		twiND ₃ ⁺ , δCCN			352 w
δCH_2	1467 s	1740 s	1467 m	?			270 sh
	1445 sb	1451 s		lattice modes			126 vs
vC-O	1431 sb	1415 sb	1418 m				86 vs

^a Not observed owing to nujol bands.

addition, the total number of bands is much lower than the maximum number expected. This fact could be explained by small inter-ion interactions in the unit cell and also in terms of the fact that all measurements were carried out on polycrystalline samples.

3.3. Vibrational spectra of MBAN

The IR spectra of M β AN recorded at laboratory and low temperatures (90 K) are depicted in Fig. 4 together with the Raman spectrum; the peak positions are listed in Table 8. The IR spectra of deuterated MBAN (recorded at 298 K and 90 K), together with the Raman spectrum, are depicted in Fig. 5 and the maxima are listed in Table 9. The overall character of the vibrational spectra is in accordance with the results of the M β AN crystal structure determination; i.e., a compound consisting of β -alaninium and nitrate ions, interconnected by a network of hydrogen bonds.

Assignment of the bands in the vibrational spectra of M β AN and its deuterated analogue was based on the results of a previous study on interpretation of the vibrational spectra of β -alanine [7, 8], nitrate [9] and the addition compounds of glycine [10].

The stretching vibrations of the N-H and O-H groups interconnected by the hydrogen bond system in the crystal appear in the IR spectrum as broad, medium-intensity bands in the $3250-2500 \text{ cm}^{-1}$ region $(2400-1800 \text{ cm}^{-1} \text{ region in the deuterated})$ compound). It is apparent from the crystal structure (Table 3) that these are hydrogen bonds of the N-H···O type with a length of 2.9-3.2 Å and of the $O-H\cdots O$ type with a length of ca. 2.6 Å. On the basis of correlation curves [11] between the wavenumber of the ν O–H vibration and the length of the hydrogen bond, the band corresponding to the O-H···O bonds can be expected at 2600 cm^{-1} . The temperature-sensitive band corresponding to out-ofplane O-H···O bending vibrations, characteristic for this type of intermediate hydrogen bond, is located at ca. 950 cm^{-1} .

The bands of the stretching vibrations of CH_2 , similar to those for β -alanine [8], were observed in the 3030–2940 cm⁻¹ region. These vibrations, which are quite intense in the Raman spectra, are almost masked in the IR spectra of natural M β AN by the broad bands of the stretching N–H and O–H vibrations. The low-intensity bands found particularly in the low-temperature IR spectrum from 2400 to 1800 cm^{-1} can be assigned to the overtones and combination bands of the fundamental vibrations.

The band of the C=O stretching vibration, which confirms the existence of the β -alaninium cation in the crystal structure, is located at 1700 cm⁻¹. When the sample temperature is decreased, it is split into two symmetric branches (probably due to interactions in β -alaninium dimers). In the deuterated compound, splitting into two bands with different intensities (1686 and 1644 cm⁻¹) was observed even at laboratory temperature. The presence of the weak satellite peaks in the 1780–1760 cm⁻¹ region can be explained by interactions between the C=O stretching vibration and overtones or combination vibrations.

The deformation vibrations of the NH₃⁺ group were recorded in the range 1630 to 1500 cm⁻¹. A great multiplication of the number of bands appears especially for antisymmetric vibrations in the Raman and low-temperature spectra. The corresponding bands of the δ ND₃⁺ vibrations were observed in the 1175– 1145 cm⁻¹ region in the spectra of the deuterated compound.

Manifestations of the deformation vibrations of the CH_2 groups can be observed from ca. 1470 to ca. 1430 cm⁻¹. The number of bands of these vibrations also increases in number on a decrease in temperature.

The presence of β -alaninium ions in the crystal structure is also reflected in the highly mixed bands of the C–O stretching vibration (ca. 1415 cm⁻¹) and the C–O–H in-plane bending vibration (ca. 1230 cm⁻¹), together with the C–O–H out-of-plane bending vibration (815 cm⁻¹).

The expected manifold multiplication of all bands of the internal vibrations of the nitrate groups (see Table 7) was not observed even in low-temperature IR spectra. Splitting is apparent only for the originally doubly degenerate vibrations v_3 (doublet) and v_4 (doublet to triplet). In order to confirm the interpretation of the NO₃⁻ internal vibrations, the spectra of the isotope-substituted compound NH₃⁺CH₂CH₂COOH ¹⁵NO₃⁻ has been studied. Shifts were observed in the bands of both branches of the v_3 vibration by about 30 cm⁻¹ towards lower wavenumbers (IR and Raman) and of the band of the v_2 vibration by 22 cm⁻¹ in the same direction (IR). The positions and character of the bands of the v_1 and ν_4 vibrations and of all the vibrational bands of β alaninium remained unchanged.

In the Raman spectra of the natural and deuterated compounds, the lattice modes are located in the region below 150 cm^{-1} .

3.4. Thermal behaviour of MBAN

Crystals of M β AN are stable in air up to a temperature of 373 K, at which they melt. The natural and deuterated compounds were further studied by DSC from a temperature of 95 K up to 370 K. No thermal effects were observed over the entire temperature interval.

The FTIR spectra (see Figs 4 and 5, Tables 8 and 9) were recorded in the temperature interval from 90 to 298 K. However, as the temperature decreases, there is only a narrowing and partial separation of the bands that is sometimes connected with minimal shifting. It is thus apparent that a decrease in temperature of the sample does not lead to any changes in the infrared spectrum that would indicate the occurrence of a structural phase transition.

4. Conclusions

According to the X-ray data, the crystal structure of M β AN consists of β -alaninium dimers (linked by two intermediate asymmetrical hydrogen bonds of length 2.64 Å) and nitrate anions connected by a system of hydrogen bonds, in which all the hydrogen atoms of the NH₃⁺ groups participate. The overall character of the vibrational spectra agrees with the results of the crystal structure solution. No evidence of a phase transition was found by DSC and low-temperature FTIR measurements over a wide interval from 90 K to the melting point temperature. M β AN crystals match the necessary symmetry condition (polar crystallographic class *mm*2) for ferroelectric materials; however, the

facts that no phase transition from ferroelectric to paraelectric phase was observed and there is no strong O–H···O hydrogen bond present in crystal structure, which is characteristic for the TGS family of ferroelectrics, leads to the conclusion that the possibility of existence of ferroelectric properties for MβAN crystals is minimal. Research of MβAN will continue with dielectric studies, which alone can decide this question.

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