

2,4,6-Triamino-1,3,5-triazin-1-ium Acetate Acetic Acid Solvate Monohydrate. Infrared and Raman Spectra

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The crystals of the new melaminium salt, *i.e.* melaminium acetate acetic acid solvate monohydrate, $C_3H_7N_6^+ \cdot CH_3COO^- \cdot CH_3COOH \cdot H_2O$, were obtained by the slow evaporation of an aqueous solution at room temperature. Powder infrared and Raman spectra were measured and interpreted. The vibrational spectra in the region of internal vibrations of ions corroborate structural data recently published by Perpétuo and Janczak.¹ Some spectral features of this new crystal are referred to corresponding one for melamine crystal as well as other melamine complexes in crystalline form. Hydrogen-bonded network present in the crystal gives notable vibrational effect.

Key Words : Melamine. Acetates. Hydrogen bonds. Vibrational spectra. Structure-spectra correlation

Introduction

The salts of acetic acid form a broad family of hydrogen bonded crystals which were intensively studied by vibrational methods.²⁻⁷ Some of them were the subject of theoretical analysis.^{8,9} The hydrogen bond strength in the $Mg(CH_3COO)_2 \cdot Zn(CH_3COO)_2 \cdot H_2O$ system was analysed by Koleva and Stoilova, quite recently.¹⁰

Melamine (2,4,6-triamino-1,3,5-triazine) has a wide application in industry. Melamine resin is used in automobile paints, which were examined by Zięba-Palus.¹¹ Crystals of melaminium salts exhibit interesting properties. Second harmonic generation was observed recently in the case of tetrakis(2,4,6-triamino-1,3,5-triazin-1-ium) bis(selenate) trihydrate⁴⁵ and 2,4,6-triamino-1,3,5-triazin-1,3-ium tartrate monohydrate,⁴⁴ while low temperature phase transitions were registered for melaminium diperchlorate hydrate⁴⁶ and melaminium butyrate.¹²

Generally, the solid-state complexation of melamine with different organic and inorganic (mineral) acids has an interesting aspect concerning the hydrogen bond system formed. Such a system comprises most frequently the weak hydrogen bonds of $N-H \cdots O$ and $O-H \cdots O$ types.¹³⁻²³ This phenomenon has a feature of self-organization process, widely reported in literature. The results obtained during analysis the structures of acetates can be used to discuss a design strategy for the engineering of crystals with pre-designed architecture.^{24,25} Carboxylic acids (exemplified by acetic acid) may be used as reliable building blocks of infinite three-dimensional networks.^{26,27} The anion can act as a bridge that actively associates with neighbouring cationic layers through directional intermolecular interactions. In the case of title crystal, according to crystallographic data,¹ the melaminium cations form planar chains interconnected by $N-H \cdots N$ hydrogen bonds. π - π interactions between the melaminium rings were supposed by Perpétuo and Janczak¹

from the comparison of the value their separation (*ca.* 3.25 Å) with the distance between π -aromatic ring system (*ca.* 3.40 Å). The acetic acid-acetate anions form columnar supramolecular aggregates through the dimeric like structure of hydrogen bonded water.

The examples of other crystals with mono-protonated melaminium cation are known.^{12,15,18,19,21,22,28,38,40,42,43} On the other hand, in some salts the melamine molecule is doubly protonated.^{13,14,20,44} It is worthwhile to mention here the structure of 3-amino-1,2,4-triazine published by Perpétuo and Janczak.⁴¹

In the context of literature data it seemed to be worthwhile to give the vibrational characterisation of crystalline melaminium acetate acetic acid solvate monohydrate in order to expand the understanding of the physical organic chemistry of the solid state containing multiple hydrogen-bonding systems.

Experimental Section

Preparation. The starting compounds, melamine (Aldrich, 99%) and acetic acid, 37% (Aldrich) were used as supplied and prepared in the ratio of 1 : 3. The dissolved acid was added to the hot solution of melamine with the help of dropper. After the solution was cooled to room temperature, it remained clear, without any precipitants. Then, the solution was purified with the aid of active charcoal. The solution slowly evaporated during a few days till the colourless and transparent crystals appeared.

Spectroscopic measurements. The vibrational measurements were carried out at room temperature. Infrared spectra were taken with a Bruker IFS-88 spectrometer in the region 4000-380 cm^{-1} while powder Fourier Transform Raman (FT-Raman) spectra were taken in the region 3600-80 cm^{-1} with an FRA-106 attachment to the Bruker IFS-88 spectrometer equipped with Ge detector cooled to liquid nitrogen temperature. Nd^{3+} :YAG air-cooled diode pumped laser of power *ca.* 200 mW was used as an exciting source. The

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Table 1. Wavenumbers (cm^{-1}) and relative intensities of the bands observed in the powder infrared and Raman spectra of the melaminium acetate acetic acid solvate monohydrate

IR	Raman	Assignment	IR	Raman	Assignment
3469vs	3449vw	NH ₂ asym stretch	1192m		O-H in-plane bend (<i>ca.</i> 2.7 Å)
3419vs		NH ₂ asym stretch	1164s	1164vw	Ring: semi-circle stretch ³⁴ and NH ₂ rock ³⁰
3371vssh		NH ₂ sym stretch	1156m		Ring: semi-circle stretch ³⁴ and NH ₂ rock ³⁰
3346vs		NH ₂ sym stretch	1115m		C-C stretch and C-N stretch and NH ₂ rock
3229vssh		O-H...O stretch, A component	1040m		Triazine ring breath ³⁰
3205vs	3193vwb	O-H...O stretch, A component	1018msh		out-of-plane CH ₃ rock
3109vs	3107vwb	N-H...N stretch, (<i>ca.</i> 3.0 Å)	1010m	1010vw	out-of-plane CH ₃ rock
3077vssh		N-H...N stretch, (<i>ca.</i> 3.0 Å)	999m		
3015vssh		C-H asym stretch	984m	980w	Triazine ring N, in-phase radial ³⁴
	2940w	C-H sym stretch	934w	932vw	C-C stretch
2861vs	2875vw		924w	924w	C-C stretch
2799msh		2 × (CH ₃ asym bend)	899w	899w	Triazine ring breath ³⁷
2693m			894m		Triazine ring breath ³⁷
2629m			864wb		H ₂ O rock
2517m		O-H...O stretch (2.76 Å), B component	814m		C-C stretch and ring-sextant out-of-plane bend ^{29, 34}
2430m		O-H...O stretch (2.99 Å), with water molecule	797wsh		C-C stretch and ring-sextant out-of-plane bend ^{29, 34}
2338m	2332vw	O-H...O stretch (2.84 and 2.85 Å), with water molecules	782s		COO in-plane bend
			739s		C=O in-plane def
2273m		O-H...O stretch (2.67 Å), with water molecule	720s		Ring bend ³⁰ and $\chi(\text{O-H}\cdots\text{O})$, <i>ca.</i> 2.76 Å
2201m			691s	690vs	Symmetric ring breath ³⁷
1932w			670s		OCO sym bend
1903wb		O-H...O stretch (2.76 Å), C component	662s		Ring: quadrant in-plane bend ³⁴
1785w			633s		C=O out-of-plane def
1737vs		C=O stretch	622s	628vw	out-of-plane OCO rock
	1719vw		605s		Ring bend ³⁰
1711vs	1714vw	C=O stretch	592s	593vw	Ring bend ³⁰
1696vs		NH ₂ bend	583s	575w	Ring bend ³⁰
1673vs		COO ⁻ asym stretch	566s	565w	Side-chain in-plane C-N bend ³⁰
1659vs	1665vw	COO ⁻ asym stretch	504wb		H ₂ O wagg
1634vssh	1613vw	H ₂ O in-plane-bend	473wsh		Combination tone: NH ₂ bend - NH ₂ rock ³⁰ and in-plane OCO rock
1575vs	1566vw	Side-chain asym C-N stretch ³⁰	460s	459vw	
1534vs		Side-chain asym C-N stretch ³⁰	444w		
1500vs	1510vw	NH ₂ bend	411w	407vwsh	OCO rock
1485vssh	1494vw	Ring: quadrant stretch ³¹ , or Ring: semi-circle stretch + exogenous C-N cont ³¹	395w	394w	Ring: quadrant out-of-plane ³⁴
1431vssh		C-O sym stretch	378vw		NH ₂ tors
1414vssh	1416vw	CH ₃ asym bend	217vw		lattice modes
1405vs		CH ₃ asym bend	193w		lattice modes
1394vs		Ring semi-circle stretch ³⁴	152wsh		lattice modes
1370vs		Ring: semi-circle stretch + exogenous C-N cont ³¹	144msh		lattice modes
1339vs	1344vw	CH ₃ sym bend	120vs		CH ₃ tors (around C-C)
1300vs		Ring: semi-circle stretch + exogenous C-N cont ³¹	106vs		lattice modes
1287vssh	1291vw	Carbonyl C-O stretch	94vs		lattice modes
1212m	1210vw	C-H in-plane bend			

Abbreviations: s – strong, w – weak, v – very, sh – shoulder, b – broad, m – medium, rock – rocking, bend – bending, breath – breathing, stretch – stretching, sym – symmetric, asym – asymmetric, tors – torsion wagg – wagging, cont – contract

incident laser excitation is 1064 nm. The scattered light was collected at the angle of 180°, resolution 2 cm^{-1} , 256 scans. Due to the poor detector response, the Raman counterparts of the infrared bands located above 3200 cm^{-1} are not

observed in the spectrum presented in Figure 2. The polycrystalline powders were achieved by grinding in agate mortar with pestle. Samples for FT-IR, as suspensions in oil, were put between KBr wafers. The powder infrared spectra

were taken in Nujol and Fluorolube emulsions to eliminate the bands originating from used oils. The measured spectra are shown in Figure 2. The wavenumbers of the bands and their relative intensities are provided in Table 1.

Assignments of the Bands and Discussion

The crystal structure of the melaminium acetate acetic acid solvate monohydrate was determined at room temperature quite recently.¹ According to data presented there the title crystal comprises mono-protonated melaminium (1+) residues, acetic acid molecules, acetate anions and water molecules, Figure 1.

Thus, the bands observed in the measured regions 4000-380 cm^{-1} (FTIR) and 3600-80 cm^{-1} (FT Raman), arise from internal vibrations of mono-protonated melaminium cations, acetate anions, acetic acid molecules and water molecules, the vibrations of O-H...O and N-H...O and N-H...N types

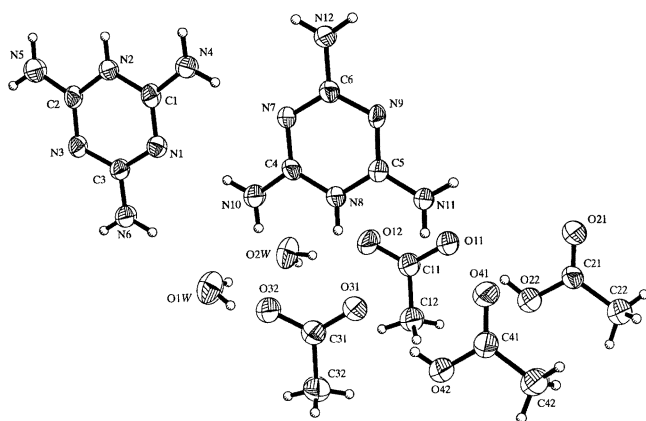


Figure 1. A view of the molecular structure of melaminium acetate acetic acid solvate monohydrate¹.

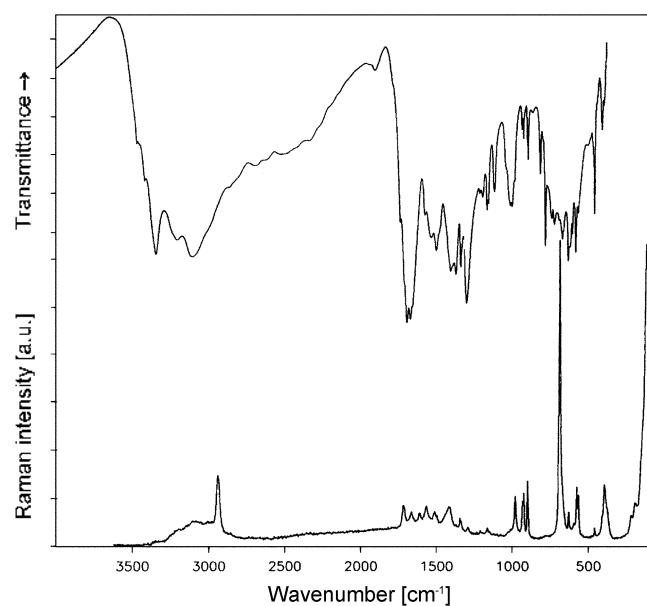


Figure 2. Room temperature powder FT IR and FT Raman spectrum of melaminium acetate acetic acid solvate monohydrate.

of hydrogen bonds and from the vibrations of lattice.

Total number (405) of optical modes may be divided into 93 lattice (45 translational and 48 librational) and 312 internal modes. This large number of internal modes may be significantly lowered taking into account that the melaminium cations ($16 \times 3 - 6 = 42$ modes), acetate anions ($7 \times 3 - 6 = 15$ modes), acetic acid molecules ($8 \times 3 - 6 = 18$ modes) and water molecules ($3 \times 3 - 6 = 3$ modes) are quite similar to each other, respectively. Nevertheless that they are symmetry related, if a factor group splitting will be neglected the number of expected bands for internal vibrations can be reduced to 78 ($42 + 15 - 18 + 3$) in both infrared and Raman spectra which is closer to the amount of observed bands in the measured spectra.

Generally we tried to give the most precise and current assignment of the bands. In some cases, however, we made, from the lack of others, the older propositions for assignment, or for comparison, we gave the older one with a new one together.

Melamine residue vibrations. Few papers concerning the melamine molecule vibrations were already published^{29-33,39} and constitute a good source for the assignment of vibrational bands.

According to crystallographic data, melaminium residues form hydrogen bonds of N-H...N and N-H...O type and the former one are much more linear than the latter one.¹ The NH_2 groups interact with the acid residue through weak N-H...O hydrogen bonds. The complex formation is reflected especially on the symmetric stretching type of vibrations of these groups. The frequency of the band originating from this type of coupling rises from 3328 cm^{-1} in the melamine crystal³⁰ to 3346 cm^{-1} in the case of studied one. The difference is equal to 18 cm^{-1} and corresponds to well known blue-shift. Similar shift is observed in the region of NH_2 bending type of vibrations. The very strong infrared band located at 1696 cm^{-1} is observed in the case of melaminium acetate acetic acid solvate monohydrate. The corresponding band for melamine crystal was observed at 1653 cm^{-1} .³⁰ Thus, the intermolecular interactions through the NH_2 groups of melamine molecule cause the rising of their frequencies for bending type of motion, also.

The most intense band in FT Raman spectrum is that at 690 cm^{-1} . This band is also quite characteristic one for all melamine complexes. It is derived from the symmetric type of vibration of triazine ring. The location of this band was analysed in several crystals.⁴⁷ The complexation of melamine causes, in all cases, the rising of the frequency of analysed vibration compared to the value for melamine alone. It is suggested, that due to number of intense ionic and donor-acceptor types of interaction with environment the sym-triazine ring becomes more rigid.

Weak Raman band at 980 cm^{-1} originates from triazine ring N in-phase radial type of vibration.³⁴ This vibration does not couple with the substituent group and can be found in the narrow 969-992 cm^{-1} region. This is an excellent Raman group frequency. Such a band is present in the FT Raman spectra of all complexes obtained by author.

The Raman band at 575 cm^{-1} with an infrared counterpart at 583 cm^{-1} was assigned to the ring bending type of vibration. In the case of melamine crystal, the corresponding Raman band is observed at 582 cm^{-1} .

The medium infrared band observed in the spectrum of melamine crystal at 1025 cm^{-1} , originating from ring breathing type of vibration, moves to the higher wavenumbers and in the spectrum of the studied salt is located at 1040 cm^{-1} . Once again, a small blue-shift is observed because the triazine ring becomes more rigid.

While the band position (814 cm^{-1}) for the ring-sextant out-of-plane bending type of vibration^{29,34} is the same in melamine as well as in the spectra of salt, in the spectrum of melaminium acetate acetic acid solvate monohydrate crystal one can notice the satellite band at about 797 cm^{-1} . The similar situation was observed in the case of melaminium butyrate crystal.¹²

The medium infrared band at 999 cm^{-1} remains unassigned. Similar medium infrared band at the same frequency is observed in the spectrum of melaminium phthalate.⁴³

For other assignments of bands originating from internal vibrations of melaminium cations, see Table I. Unfortunately, for some melamine bands the precise assignment remains an open question.

The vibrations of acetate anions and acetic acid molecules. Heyns³⁵ assumed C_{2v} molecular symmetry for CH_3COO^- ion with a free rotation of CH_3 around C-C bond. On this basis the normal vibrations can be assigned. In the triclinic lattice, the acetate ions occupy C_1 sites and one could not expect the correlation field splitting in the infrared and Raman spectra. However, in the case of more than one acetate ion in the lattice, more sets of the internal modes are expected, corresponding to the number of the crystallographically different ions. This can be exemplified by two neighbouring bands located at 1737 and 1711 cm^{-1} originating from C=O stretching type of vibrations. Similarly, two very strong infrared bands at 1673 and 1659 cm^{-1} are observed for the asymmetric stretching type of vibrations of ionised (COO^-) carboxylic groups.

The vibrations of hydrogen bonds and water molecules. The determination of the structure of hydrogen bonds from X-ray data is useful for the interpretation of vibrational spectra. According to Perpétuo and Janczak,¹ there are twenty hydrogen bonds of O-H...O, N-H...O and N-H...N type. Each type covers different range of lengths with different average value of length. The shortest one are hydrogen bonds of O-H...O type. They cover the range of $2.581\text{--}2.993\text{ \AA}$ with the average value equals to 2.760 \AA . They are also mostly differentiated. The medium are N-H...O type in the range of $2.746\text{--}3.085\text{ \AA}$ with the average value equals to 2.885 \AA . The longest one are of N-H...N type. They cover the range of $2.982\text{--}3.008\text{ \AA}$ with the average value equals to 2.999 \AA . The position of infrared band originating from the absorption of particular hydrogen bond strongly depends on their length.³⁶ Therefore, one can divide all hydrogen bonds into groups. On the basis of such a division, the bands corresponding to each group of bonds are

considered in Table I.

According to the structural data, the water molecules act as a proton donors and proton acceptors (cooperative effect). Four infrared bands, medium in intensity, located at 2430 , 2338 , 2273 and 2201 cm^{-1} are seen in the spectrum (Fig. 2). They were attributed to the vibrations of hydrogen bond formed by the water molecules. The weak and broad infrared band observed at 864 cm^{-1} was attributed to rocking type of vibrations of water molecules. The analogous band is observed in infrared spectrum of melaminium bis(4-hydroxybenzenesulphonate) dihydrate crystal.⁴⁷

Summary

Melaminium acetate acetic acid solvate monohydrate has been chosen to study by infrared and Raman spectroscopy due to interesting hydrogen bond system formed. Generally, vibrational spectra support structural data published by Perpétuo and Janczak.¹ For internal vibrations of mono-protonated melaminium cations, most bands corresponding to theoretical literature data were assigned. Some bands are shifted comparing to their analogues in melamine crystal. This is a consequence of intermolecular interactions between melaminium cations, acetate anions and the molecules of acetic acid and water. Due to weak interactions of O-H...O and N-H...O and N-H...N type, which manifest themselves as perturbed amino group vibrations of mono-protonated melaminium cations, the corresponding infrared band at 3346 cm^{-1} is shifted towards higher frequency comparing to the melamine crystal (3328 cm^{-1}). The analysis of hydrogen bonds existing in studied crystal shows that a driven interactions may be these hydrogen bonds, in which hydrogen atom bounded to ring nitrogen of s-triazine participates. Such a hydrogen bonds are always most linear ($163\text{--}169^\circ$). It is supposed, that a directionality of hydrogen bonds is manifested in such intermolecular interactions.

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