INFRARED AND RAMAN SPECTRA OF MELAMINIUM BIS(4-HYDROXYBENZENESULFONATE) DIHYDRATE

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Abstract

Room temperature powder infrared and Raman measurements for the new melaminium salt, 2,4,6-triamino-1,3,5-triazine-1,3-diium bis (4-hydroxybenzenesulfonate) dihydrate, $C_3H_8N_6^{2+}\cdot 2C_6H_5O_4S^{-}\cdot 2H_2O$, crystal were carried out. The vibrational spectra corroborate the X-ray data recently published by Janczak *et al*. Some spectral features of this new crystal refer to corresponding ones for other melamine complexes. No detectable signal was observed during powder test for second harmonic generation. DSC performed for the crystal shows no phase transition in the studied temperature range (113-293 K).

Introduction

Following the dimer of cyanamide, the trimer *i.e.* melamine (2,4,6-triamino-1,3,5-triazine) is interesting for crystal engineering[1] or supramolecular chemistry.[2] In order to better understand the behaviour of melamine molecule, the vibrational characterization of a new melaminium salt of 4-hydroxybenzenesulfonic acid was performed.

The organic salts of 4-hydroxybenzenesulfonic acid are interesting because some of them exhibit nonlinear optical properties like second harmonic generation. This phenomenon was already observed by author in the case of other crystals containing SO_3 groups *i.e.* melamine with aminomethanesulfonic acid, aniline with *p*-toluenesulfonic acid and L-lysine with *p*-toluenesulfonic acid.[3] The structural and vibrational studies of the crystals comprising similar organic or inorganic parts can be useful in elucidation of the role of these molecular units in the generation of second harmonic frequency of light (SHG). Therefore it seemed to be worthwhile to characterize title crystal with the help of infrared, Raman, calorimetric and preliminary second harmonic powder measurements.

A few papers with assignments of internal vibrations of melamine molecule were already published.[4-10] The fundamental frequency assignment for melamine and

melamine d_6 were done almost 50 years ago in the classical paper of Jones and Orville-Thomas.[5] Some of aforementioned works were devoted to the band assignment for melamine and hexa-methoxymethyl melamine.[6] Few of the fundamentals were assigned in the paper of Meier *et al.*[7] He also presented the form of some of the normal modes of methylol melamine.

The crystal structure of the melaminium bis(4-hydroxybenzenesulfonate) dihydrate was determined at room temperature recently.[11] According to data presented there the title crystal comprises doubly protonated melaminium (2+) residues, dissociated *p*-phenolsulfonate anions and water molecules. Generally, the solid-state complexation of melamine with different organic and inorganic (mineral) acids has an interesting aspect concerning the formed hydrogen bond system. Such a system comprises most frequently the N-H···O and O-H···O types.[11-14] This phenomenon has features of self-organization process widely reported in literature.

Sulfonates are hydrophilic. The title crystal, grown from an aqueous solution, contains water molecules and has complicated hydrogen bond networks, similar to the others.[15-18] The SO_3 groups, which are present in title crystal, play an important role in *e.g.* the complexation of polymer electrolytes. NMR studies performed on complex of poly(propylene oxide) with sodium trifluoromethanesulfonate[19] confirmed the vibrational spectroscopic studies, showing that $CF_3SO_3^-$ anion is involved in a great deal of cation-anion association.

Results and discussion

Assignment of the bands

The bands observed in the measured region 4000-380 cm^{-1} arise from the vibrations of protons in the hydrogen bonds, the internal vibrations of the *p*-phenolsulfonate anions, the internal vibrations of melaminium cations and from the vibrations of water molecules. The bands below 200 cm^{-1} in the Raman spectrum arise from the lattice vibrations of the crystal.

The vibrations of melaminium residues. For the melamine alone, some bands found in our infrared and Raman spectra were not observed by Schneider *et al.*[8] For infrared bands they are as follows: 2982ssh, 2828s, 2678m, 2332w, 2195w, 1761w,

1308m, 872w, 751w, 442wsh, and for Raman: 881vw, 822vw, 570vw, 250vw, 156vs, 149s, 139m, 124vs, 110w and 100vs. Only one band observed by Schneider in melamine powder infrared spectrum, *i.e.* at 1075wb, is not present in our spectrum.

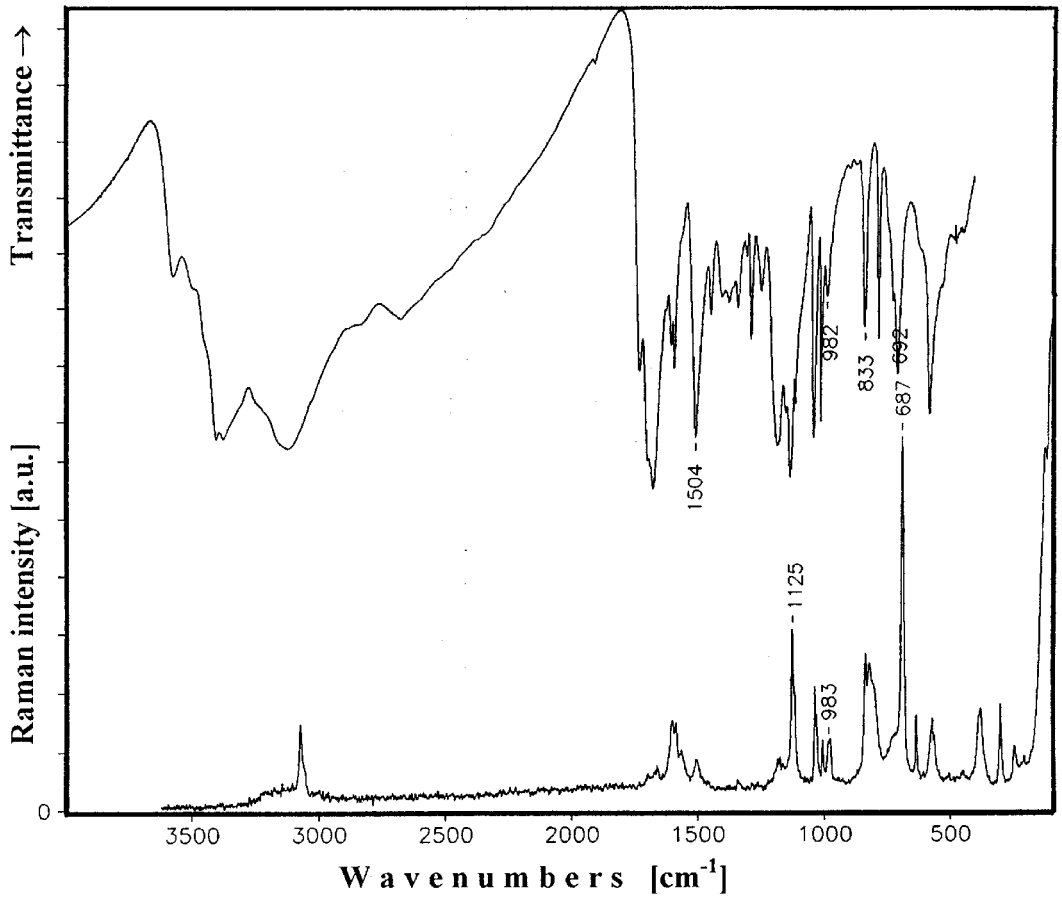

Fig. 1. Room temperature powder FT-IR and FT-Raman spectra of melaminium bis(4-hydroxybenzenesulfonate) dihydrate crystal.

Very weak Raman band at 983 cm^{-1} originates from triazine ring N in-plane radial vibration.[9] This is suitable Raman group frequency. This vibration does not couple with the substituent groups and can be found in the 969-992 cm^{-1} region. Such a band is present in fact in the FT-Raman spectra of all other complexes obtained by author. In the complex of melamine with: acrylic acid at 981 cm^{-1} a very weak band, butyric acid at 982 cm^{-1} a very weak band, glutaric acid at 977 cm^{-1} a weak band, arsenic acid at 978 cm^{-1} a very weak band, phthalic acid at 984 cm^{-1} a very weak band, glycolic acid at 985 cm^{-1} a very weak band and perchloric acid at 982 cm^{-1} a weak band.

Table 1. Wavenumbers (cm^{-1}) and relative intensities of the bands observed in the powder infrared and Raman spectra of the melaminium bis(4-hydroxybenzenesulfonate) dihydrate crystal.

FT-IR	FT-Raman	Assignment	Reference
3573m		H_2O asym stretch	
3493m		H_2O sym stretch	
3438msh		NH_2 asym stretch	
3401s		NH_2 asym stretch	
3373s		NH_2 sym stretch	
3232ssh			
3206ssh	3212vwb	O-H···O stretch, 2.91 and 3.00 Å	
3162vssh	3176vw	Combination tone: NH_2 bend + side-chain asym C-N stretch,	5
3118vsb	3118vwb	N-H···O stretch, 2.85-2.94 Å	
	3072w	C-H stretch	
	3060vwsh	C-H stretch	
2837mb		N-H···O stretch, 2.79 Å	
2674mb		Combination tone: NH_2 asym stretch - side chain out-of-plane C-N bend and N-H···O stretch, 2.70 Å	5
1727s		NH_2 bend	
1694vs	1699vw	NH_2 bend	
1685vs		NH_2 bend	
1672vs	1661vw	NH_2 bend	
1639ssh		NH_2 bend	
1622m		Ring: quadrant stretch; NCN bend + ring def	6 23
1600m	1601w	H_2O def	
1588m	1585w	H_2O def	
1561wsh	1565vw	Side-chain asym C-N stretch, ring: quadrant stretch, NCN bend + ring def and NH_2 sciss	5 6 23
1512msh		NH_2 def	
1504vs	1505vw	NH_2 def	
1442m		Ring stretch, ring and side-chain C-N stretch	5 23
1397m			
1370m		Ring: semi-circle stretch + exogenous C-N contract	6
1354m		Ring: semi-circle stretch	9
1335m	1342vw	Ring: semi-circle stretch	9
1303m		Ring: semi-circle stretch + exogenous C-N contract	6
1299m		Ring: semi-circle stretch + exogenous C-N contract	6
1283m		C-H def	
1254msh			

Table 1. *Continued on the next page.*

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1243m		SO_3 asym stretch	
1179vs	1184vw	SO_3 asym stretch	
1173vs	1174vw	SO_3 asym stretch	
1144s	1141vwsh		
1129vs	1125m	SO_3 asym stretch	
1119vssh	1116w		
1107s	1107vwsh		
1086msh		NH_2 tors	
1036s	1037w	SO_3 sym stretch	
1031s	1030w	SO_3 sym stretch	
1006s	1006vw	NH_2 swing and SO_3 asym stretch	23
982m	983vw	Triazine ring N, in-phase radial	9
975msh	975vw		
963m		Ring breath	23
918w		Ring breath	23
890w		Ring breath	23
864w			
846wsh		CCC def	
839wsh	837w	Ring def. (out-of-plane)	23
833m		CNC def	
827msh	822w		
819wsh	819w		
	810w	Ring-sextant out-of-plane bend	9
	805w		
778m	779vw	Side-chain out-of-plane C-N bend, ring-sextant out-of-plane bend	5 9
736msh	730vwb	Ring def. (out-of-plane)	23
702s		CCO def	
692msh	687vs	Ring breath and NH_2 bend and C-S stretch	23
	635w		
607mb		H_2O twist	
580ssh	578wsh	SO_3 asym def	
575s	572w	Ring bend, NH_2 and CNH bend	5 23
564ssh	563vw	SO_3 asym def	
553msh		NH_2 swing and SO_3 def	23
530m		Side-chain in-plane C-N bend and SO_3 sym def	5
439wb	451vwb	SO_3 sym def	

Table 1. *Continued on the next page.*
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387wsh	NH_2 tors and SO_3 rock	23
380w	Ring: quadrant out-of-plane	9
300w		
244vw		
218vw	Side-chain out-of-plane bend	23
204vw		
135ssh	Lattice vibration	
119s	Lattice vibration	
98vs	Lattice vibration	

Abbreviations:
s – strong, w – weak, v – very, sh – shoulder, b – broad, m – medium, tors – torsional, asym – asymmetric, sym – symmetric, bend – bending, rock – rocking, def – deformation, swing – swinging, twist – twisting, stretch – stretching, breath – breathing, scis – scissoring, contract – contracting.

The medium band located at 833 cm^{-1} in the infrared spectrum of title crystal was attributed to CNC deformations of melamine ring.

The most intense band in FT-Raman spectrum is at 687 cm^{-1}. This band is also a very characteristic one for all melamine complexes. It originates from the symmetric vibrations of sym-triazine ring. The location of this band was analysed by author in several crystals and the results are derived in Table 2.

As it follows from the data presented in Table 2, the complexation of melamine causes, in all cases, the rising of the frequency of analysed vibration compared to the value for melamine alone. For some melamine bands the precise assignment remains an open question.

The vibrations of p-phenolsulfonate anions. For isolated SO_3 group with C_{3v} symmetry one expect four normal modes: $\nu_3(E) = 1291\ cm^{-1}$ (asym stretch), $\nu_1(A_1) = 1053\ cm^{-1}$ (sym stretch), $\nu_4(E) = 551\ cm^{-1}$ (asym def) and $\nu_2(A_2) = 535\ cm^{-1}$ (sym def). In the studied crystal, the sulfonate group has a slightly distorted tetrahedral geometry[11]. Due to the lowering of the symmetry from an ideal C_{3v} configuration and the crystal field effect, the splitting can be observed for double degenerated ν_3 and ν_4 modes.

In the infrared spectra of the *p*-phenolsulfonic acid, three very strong bands at 1218, 1172 and 1125 cm^{-1} are present[3], which unambiguously originate from asymmetric stretching vibrations of SO_3 groups.

Table 2. The position of the Raman band originating from the symmetric ring breathing vibration in different crystalline complexes of melamine. In melamine either purchased or recrystalized from water solution this band is located at 676 cm^{-1}.

Proton donor	Position of the band in non-deuterated crystal [cm^{-1}]	Position of the band in deuterated crystal [cm^{-1}]	Reference
m-nitrophenol	679		3
boric acid	680		3
L-tartaric acid	683	653	24
2,5-dinitrophenol	684	652	3
iodic acid	684		3
trichloroacetic acid	684		3
terephthalic acid	684		3
phthalic acid	685		25
phosphoric acid	685		26
arsenic acid	686		3
selenic acid	686	651	27
p-toluenesulfonic acid	686		3
glycolic acid	686		3
butyric acid	687		28
valeric acid	687		3
maleic acid	687		3
glutaric acid	687		3
sulphuric acid	688		29
perchloric acid	688		3
methanesulfonic acid	688		3
selenous acid	688		3
phosphorous acid* (form with νP-H band at 2358 cm^{-1})	689		3
phosphorous acid* (first crystallization)	689		3
hydrochloric acid	690		30
acetic acid	690		31
malic acid	690		3
acrylic acid	690		3
phosphorous acid* (after recrystallization)	691	654	3
nitric acid	691	653	3
oxalic acid	692		3
citric acid	695		32

* different forms of crystals were obtained with phosphorous acid.

Thus the bands observed in the infrared spectra of title compound at 1243, 1179, 1173 and 1129 cm^{-1} were attributed to these vibrations. It was worthwhile noticing that in the crystalline complex of L-lysine with *p*-phenolsulfonic acid[3] similar bands are observed in the infrared spectrum at 1242, 1165 and 1120 cm^{-1}. Similarly, three strong bands at 1036, 1031 and 1006 cm^{-1} in infrared spectrum of title crystal originate from symmetric stretching vibrations of SO_3 groups. Quite similar pattern is observed at 1027, 1022 and 1003 cm^{-1} in the complex of L-lysine mentioned above.

The strong band at 564 cm^{-1} observed in infrared spectrum having a very weak Raman counterpart at 563 cm^{-1} was attributed to SO_3 deformation vibrations. Similar strong band can be noticed at 568 cm^{-1} in the infrared spectrum of the L-lysine complex mentioned above.

The strong band observed in infrared spectrum at 702 cm^{-1} can be assigned to CCO deformation of phenol ring. In the infrared spectrum of L-lysine complex the corresponding band was found at 695 cm^{-1}. Additionally, the CCC deformations of phenol ring give the weak band at 846 cm^{-1} that corresponds to the band at 850 cm^{-1} in the complex of L-lysine with *p*-phenolsulfonic acid.

Sun *et al.*[20] published the structure and FT-IR spectra of caesium 4-methyl-benzenesulfonate and the spectra of 4-methylbenzenesulfonic acid monohydrate. Our assignments for anion are in good correspondence with presented in the paper mentioned above.

The vibrations of water molecules The eight water molecules in the elementary unit cell[11] of the title crystal are involved as donors in hydrogen bonds with SO_3^- groups and as acceptors in hydrogen bonds with hydroxyl group of phenol ring and amino group from melaminium residue. These hydrogen bonds are relatively weak, with the lengths of 2.905, 2.997, 2.786 and 2.846 Å, respectively.

Two medium intensity bands at 3573 and 3493 cm^{-1} in infrared spectrum were assigned to the antisymmetric and symmetric stretching vibrations of water molecules. Their Raman counterparts are not visible on the spectrum presented in Fig. 1 because the inherent scattering intensity of these modes is low like in all H-bond systems.

The bands corresponding to in-plane deformation vibrations were found at 1600 and 1588 cm^{-1} (infrared, medium intensity) and at 1601 and 1585 cm^{-1} (Raman, weak bands).

The infrared medium and broad band located at 607 cm^{-1} was assigned to rocking vibrations of water molecules.

The hydrogen bonds vibrations. Janczak and Perpétuo[11] found that there are two types of hydrogen bonds in the crystal under study: O-H···O with the length of 2.786 Å and four of N-H···O type with the lengths of 2.699, 2.846, 2.901 and 2.945 Å, respectively. The vibrations of the latter one manifest themselves as perturbed amino group vibrations of the dissociated melaminium di-cation. Moreover, the hydrogen atoms of water molecules are involved in O-H···O hydrogen bonds with the lengths of 2.997 and 2.905 Å.

The shoulder at 3438 cm^{-1} and the band at 3401 cm^{-1} observed in infrared spectra originate from the asymmetric stretching vibrations of three NH_2 groups. All six protons of these groups are engaged in weak interactions mentioned above. The symmetric stretching vibrations of these groups give a very strong and broad band in infrared spectrum, located at 3737 cm^{-1}.

Weak interactions through hydrogen bonds give broad and intense absorption around *ca.* 3100 cm^{-1} with several submaxima. The proposed assignments for particular hydrogen bonds are given in Table 1.

Lattice vibrations. Only two bands and one shoulder are observed in the FT-Raman spectrum in the range of lattice vibrations *i.e.* for the wavenumbers lower than 200 cm^{-1}. A very strong band is present at 98 cm^{-1} and the strong band at 119 cm^{-1} with a strong shoulder at *ca.* 135 cm^{-1}. It seemed worthwhile mentioning here, that the lattice dynamics was studied for bis(4-chlorophenyl)sulfone by Criado,[21] and the calculated infrared and Raman frequencies were compared with experimental data.

Second harmonic generation

The measurements were performed before the structure was known. During the powder SHG test of the crystal presented here no detectable signal was observed. It is in consistency with the X-ray experiments giving centrosymmetric *Pbcn* space group (No. 60) of orthorhombic system.[11] For centrosymmetric crystals second harmonic frequency of light should not be observed.[22]

DSC calorimetric studies

DSC measurements performed for melaminium bis(4-hydroxybenzenesulfonate) dihydrate crystal do not indicate the occurrence of the phase transition in the studied temperature range (113-293 K).

Conclusions

Most infrared and Raman bands corresponding to calculated vibrations of melamine molecule reported in literature were tentatively assigned. Generally, vibrational spectra support structural data. Low temperature phase transition was not observed. SHG signal was not detected confirming centrosymmetric structure of the complex.

Experimental

Preparation. The starting compounds, melamine (Aldrich, 99%) and 4-phenolosulfonic acid (FERAK LABORAT GMBH BERLIN, pure) were used as supplied and prepared in the ratio of 1:3. The dissolved acid was added to the hot solution of melamine (2g) with the use 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 carbon. 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 on a Bruker IFS-88 spectrometer in the region 4000-80 cm^{-1}. Resolution was set up to 2 cm^{-1}, signal/noise ratio was established by 32 scans, weak apodisation. Powder Fourier Transform Raman (FT-Raman) spectra were taken 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.* 200mW was used as an exciting source. The incident laser excitation is 1064 nm. The scattered light was collected at the angle of 180° in the region 3600-80 cm^{-1}, resolution 2 cm^{-1}, 256 scans.

The polycrystalline powders were obtained by grinding in agate mortar with pestle. Samples, as suspensions in oil, were put between KBr plates. The powder infrared

spectra were taken in Nujol and Fluorolube emulsions to eliminate the bands originating from used oils. The infrared spectrum of *p*-phenolosulfonic acid was obtained as a film without oils.

Differential scanning calorimetry measurements. DSC was carried out on a Perkin Elmer DSC-7 calorimeter equipped with a CCA-7 low temperature attachment with a heating/cooling rate of 20 K/min. The sample of the mass *ca.* 26 mg was sealed in the aluminium caps.

SHG powder test. Preliminary SHG experiment was carried out on powder sample, which was simply irradiated at 1064 nm by a Q-switched pulsed Nd:YAG laser.

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Povzetek

Posneli smo infrardeče in Ramanske spektre polikristaliničnih, do sedaj še nepoznanih melaminskih soli $C_3H_8N_6^{2+}\cdot 2C_6H_5O_4S^-\cdot 2H_2O$. Ugotovili smo, da vibracijski spektri podpirajo rezultate dobljene iz spektrov narejenih z difrakcijo X-žarkov, ki jo je nedavno tega objavil Janczak s sodelavci. Nekateri vibracijski trakovi v spektrih na novo sintetiziranih spojin se ujemajo s trakovi drugih melaminskih kompleksov, vendar so testi pokazali, da spojine ne izsevajo višjih harmonskih nihanj. V temperaturnem območju 113-293 K spojine ne kažejo fazne spremembe, kot to potrjujejo DSC merjenja.